THE JOURNAL
OF
CHEMICAL PHYSICS

VOLUME 1 APRIL, 1933 NUMBER 4

On the Theory of the Structure of CH_4 and Related Molecules: Part II

J. H. VAN VLECK, *Department of Physics, University of Wisconsin*

(Received January 30, 1933)

Explicit calculations are made to examine whether the tetrahedral model of CH_4 is really the most stable in the Hund-Mulliken and Slater-Pauling theories. The secular determinant involved in the H-M procedure is too complicated (degree 8) to solve generally, but three methods of approximation are given applicable in three different limiting cases, in all of which the tetrahedral model proves to be that of least energy quite irrespective of repulsions between the H atoms. The fact that two of the methods do not assume the carbon *s-p* separation to be small shows that *s-p* hybridization is not a necessary condition for tetrahedral valence bonds. Calculations are also given which show that in the Heitler-London-Pauling-Slater method the regular tetrahedron is superior to other models of somewhat lower symmetry. It is further calculated according to both the H-M and H-L-P-S schemes that in compounds of the form CH_2X_2, CHX_3, and CH_3X, the most stable models are tetrahedra of less symmetry than the regular tetrahedron; i.e., models with the valence angles somewhat distorted from 109.5° unless the C−H and C−X bonds are of equal intensity. The predicted directions of the deviations from 109.5° are in agreement with x-ray diffraction data for CH_2Cl_2 and $CHCl_3$. The conclusion is rather prevalent in the literature that with *s-p* hybridization and electron pairing two bond axes tend to set themselves at 109.5°. This is shown incorrect; instead the angle can be anything between 90° and 180° depending on the relative intensities of the *s* and *p* bonds. If the *s* bonding power is not negligible, the angle between an NH axis and the pyramidal axis in NH_3 should be somewhat greater than the value 54.7° which is obtained if the three NH axes are orthogonal and which is characteristic of pure *p*-bonding. Actually Dennison and Uhlenbeck find 68°, and Lueg and Hedfeld 73°, from band spectra. It is shown that CH_4^+ should be a flattened rather than regular tetrahedron, conceivably even being plane. Also CH_3 should be a flatter pyramid than NH_3.

IN Part I[1] a general comparison was given of the Hund-Mulliken and Slater-Pauling[2] theories of valence in carbon compounds. It was shown that the H-M procedure gives excessive accumulation of electrons on one atom, while the S-P viewpoint loses rather too much of the symmetry properties characteristic of an individual electron in fields of tetrahedral symmetry. We do not intend these remarks as disparaging criticisms, for insuperable mathematical difficulties prevent any really accurate solution, and both methods are to be admired for the headway they have made in the understanding of carbon valencies. However, since none of the procedures are strictly correct, unless modified by exceedingly difficult higher approximations, it appears desirable as one aim of the present paper to prove that the tetrahedral model of CH_4 is the most stable by as many methods as possible, rather than to accept such a model solely because of the tetrahedral geometry of the sp^3 wave functions of Pauling and Slater. If, as it turns out, the tetrahedral configuration invariably has the least energy in the various feasible limiting cases represented in the different theories, we can feel reasonably sure that this configuration is also the best in the intractable intermediate case actually realized. Although we

[1] J. H. Van Vleck, Part I, J. Chem. Phys. **1**, 177 (1933).
[2] See Part I for references to the literature.

shall give most of our space to the H-M scheme of attack (Sections 1–4), we do not wish to convey the impression that it is superior to the H-L-P-S one (Section 5). The H-M procedure is adaptable formally to a greater variety of models, but the H-L-P-S is probably more satisfactory if numerical success is desired. For numerical rather than formal results, everything in the H-M method would depend on a happy choice of a self-consistent field.

Before proceeding to the details of the calculations we shall state certain simplifications which we shall make throughout without further mention. We shall neglect all types of forces between H atoms, notably the Coulomb repulsions of the H nuclei in polar models, and terms due to mutual overlapping of the H wave functions. These H-H forces are doubtless repulsive,[3] and so only accentuate the stability of the tetrahedral model since in the tetrahedron the H atoms are evidently in the aggregate as far separated as possible. It is, however, of interest to show that the tetrahedral model evolves itself in virtue of the directional valence of the central C atom without invoking any H-H repulsions. To avoid excessive complexity, it will be supposed that all four H atoms are equidistant from the C atom. We shall always make the usual neglect of excited states of the C and H atoms. That is to say, we assume that in expanding the complete wave function in terms of unperturbed C and H wave functions, the coefficients of the 3,4..quantum states of C and 2,3..quantum states of H are comparatively small. Consideration of these higher states would be required if we were to include corrections for polarization. The very small bonding effect of the K shell of carbon will be disregarded.

1. First Stages of Calculation According to Generalized Hund Method

Following Hund, we shall assume that the molecular wave functions of CH_4 can be expressed to a sufficient approximation as linear combinations of the eight wave functions

$$\psi(1s;\mathrm{H}_i),\ (i=a,b,c,d);\qquad \psi(2s;\mathrm{C}),\qquad \psi(2p\sigma_x;\mathrm{C}),\qquad \psi(2p\sigma_y;\mathrm{C}),\qquad \psi(2p\sigma_z,\mathrm{C}).\quad (1)$$

Here $\psi(2p\sigma_x;\mathrm{C})$ means a carbon $2p$ state which has $m_l=0$ when viewed along the x axis. The functions (1) are to be taken as solutions of the equations

$$[\nabla^2+(8\pi^2m/h^2)(W_k{}^C-V_C)]\psi(2k;\mathrm{C})=0\ (k=s\text{ or }p),\quad [\nabla^2+(8\pi^2m/h^2)(W^H-V_{H_i})]\psi(1s;\mathrm{H}_i)=0,\quad (2)$$

where V_H and V_C are the potential energies of an electron in the field of an H and C atom, respectively. These potential energies need not be considered those due to a bare H nucleus and a C nucleus surrounded by $-6e$, but rather these nuclei surrounded by an appropriately chosen centro-symmetric electron density clouds, so that $\psi(1s;\mathrm{H})$ is not necessarily an ordinary hydrogenic wave function. The question of the best choice of the cloud need not concern us, as our aim is a proof of the tetrahedron's stability rather than numerical calculation of the binding energy. The cloud screening the C nucleus will be greater than $-6e$ if it attracts much charge from the H atoms, making the molecule appreciably polar. The choice of the screening cloud must, for tractability, be taken independent of the spatial arrangement of the H atoms. It may be urged that the "best cloud" does actually depend on the arrangement; but this does not vitiate our proof, since with any given cloud we will prove the tetrahedral model that of least energy. The embodiment of electron repulsions through a statistical charge density or cloud is essentially the Hartree method of the self-consistent field except that, as noted to the writer by Professor Kramers, our procedure does not represent the Hartree method in its full generality. Hartree uses different clouds for obtaining different solutions corresponding to various classes of electron orbits, whereas we must use the same screening cloud for all eight solutions of our forthcoming secular problem.

We shall use the following notation for integrals which will enter in the construction of the secular determinant:

[3] Cf. Heitler and Rumer, Zeits. f. Physik **68**, 12 (1931) and discussion to be given in Part III.

$$\left.\begin{aligned} B &= \int\int\int \psi(1s;\mathrm{H}_i)^2 V_C dv, & C_k &= -\int\int\int \psi(2k_i;\mathrm{C})^2 V_{H_i} dv, \\ D &= -\int\int\int \psi(2s;\mathrm{C})\psi(2\sigma_i;\mathrm{C})\, V_{H_i} dv, & Q_k &= -\int\int\int \psi(1s;\mathrm{H}_i)\psi(2k_i;\mathrm{C})\, V_{H_i} dv, \\ R_k &= -\int\int\int \psi(1s;\mathrm{H}_i)\psi(2k_i;\mathrm{C})\, V_C dv, & T_k &= \int\int\int \psi(1s;\mathrm{H}_i)\psi(2k_i;\mathrm{C}) dv, \end{aligned}\right\} \tag{3}$$

with $k=\pi$, σ, or s. Note that $Q_\pi = R_\pi = T_\pi = 0$.

The notation π_i, σ_i means that the spatial quantization is relative to the axis $\mathrm{C}-\mathrm{H}_i$, and the indices $p\pi$, $p\sigma$ are here and henceforth abbreviated to π, σ. A π state has $m_l^2=1$; a σ state $m_l=0$. The vanishing of Q_π and R_π follows from the axial symmetry of V_{H_i}, V_C on integrating over the azimuthal coordinate φ involved in $dv = r^2 \sin\theta dr d\theta d\varphi$. The integrals are independent of i because all four H atoms are equidistant from C.

The expressions C, D, Q, T, defined in (3) may all be considered positive. Here and elsewhere we omit subscripts when our remarks apply collectively to the π, σ, and s types. It is true that some of the integrals are really arbitrary in sign because of arbitrary phase factors in the wave functions, but the final formulas which we shall obtain for the energy will naturally involve these expressions only through products (e.g., $Q_\sigma T_\sigma$) which are invariant of the choice of phases. It is convenient, however, to take these expressions individually positive. To see that this is possible, one notes that $\psi(1s;\mathrm{H}_i)$ is nodeless and so may be taken everywhere positive, while $\psi(2s;\mathrm{C})$, $\psi(2\sigma_i;\mathrm{C})$ can be taken positive where they overlap the atom H_i, which will be well beyond the node of $\psi(2s;\mathrm{C})$. The potential energy V_{H_i} is, of course, everywhere negative, since the charge screening the H nucleus is surely less than that of a proton. The signs of B, R are immaterial for our purposes.

The model will not be assumed tetrahedral. Instead it will be supposed that an axis $\mathrm{C}-\mathrm{H}_i$ ($i=a, b, c, d$) has arbitrary direction cosines l_i, m_i, n_i. The secular equation is then

$$\begin{vmatrix} E & s_l & s_m & s_n & q & q & q & q \\ s_l & F_l & r_{lm} & r_{ln} & a_l & b_l & c_l & d_l \\ s_m & r_{lm} & F_m & r_{mn} & a_m & b_m & c_m & d_m \\ s_n & r_{ln} & r_{mn} & F_n & a_n & b_n & c_n & d_n \\ q & a_l & a_m & a_n & G & 0 & 0 & 0 \\ q & b_l & b_m & b_n & 0 & G & 0 & 0 \\ q & c_l & c_m & c_n & 0 & 0 & G & 0 \\ q & d_l & d_m & d_n & 0 & 0 & 0 & G \end{vmatrix} = 0, \tag{4}$$

with the abbreviations

$$\left.\begin{aligned} a_l &= l_a[-Q_\sigma + (W_p{}^C - W)T_\sigma], & q &= -Q_s + (W_s{}^C - W)T_s, \\ E &= W_s{}^C - 4C_s - W, & F_l &= W_p{}^C - 4C_\pi + (C_\pi - C_\sigma)\textstyle\sum_i l_i^2 - W, \\ G &= W^H + B - W, & r_{lm} &= -(C_\sigma - C_\pi)\textstyle\sum l_i m_i, \qquad s_l = -D\textstyle\sum l_i. \end{aligned}\right\} \tag{5}$$

It is to be understood that $b_m, \cdots d_n$ denote expressions similar to that in (5) for a_l except that $m_b, \cdots n_d$ replace l_i. Analogous remarks apply to the rest of the notation (5).

That the direction cosines enter in the way that they do in (4) follows from the fact $\psi(2s;\mathrm{C})$ is centro-symmetric, and that the wave functions $\psi(2\sigma_x;\mathrm{C})$, $\psi(2\sigma_y;\mathrm{C})$, $\psi(2\sigma_z;\mathrm{C})$ are of the form $xf(r)$, $yf(r)$, $zf(r)$, and hence transform from one coordinate system to another like the components

of a vector.[4] For instance

$$\psi(2\sigma_x;\,\mathrm{C}) = l_i\psi(2\sigma_i;\,\mathrm{C}) + (1-l_i^2)^{\frac{1}{2}}\psi(2\pi_i;\,\mathrm{C}). \tag{6}$$

Eqs. (5) show that terms $-WT_s$, $-WT_\sigma$ involving W appear off the diagonal in (4). Such terms have arisen because the C and H wave functions are not orthogonal. In place of the formula for q in (5) we could equally well have set $q=-R_s+(W_i^H-W)T_s$, as Eqs. (2) and the self-adjoint property of the Hamiltonian operator **H** give us the relation

$$W_s^C T_s - Q_s = \int\int\int \psi(1s;\,\mathrm{H}_i)\mathbf{H}\psi(2s;\,\mathrm{C})dv = \int\int\int \psi(2s;\,\mathrm{C})\mathbf{H}\psi(1s;\,\mathrm{H}_i)dv = W^H T_s - R_s. \tag{7}$$

Analogous remarks apply to the definitions of a, b, c, d. We are using only real wave functions, which involves no loss of generality in the absence of magnetic forces. Hence (4) is symmetric as well as Hermitean.

Eq. (4) differs from Eq. (2) of Part I only in the system of representation, as (2) of I was based on sp^3 functions for carbon instead of the usual nonhybridized functions (1). The zero elements occurring in (4) are due to our agreement to neglect H-H forces.

Twice the sum of the four lowest roots of (4) is the energy of the CH_4 molecule. The sum is to be doubled because the Pauli principle allows two electrons to each solution of the orbital wave equation, so that only four roots in all are needed to absorb the eight electrons available from the H atoms and the L shell of C.

Eq. (4) is still too complicated to solve except with simplifying assumptions.

2. The "Near-ionic" Case $W^H - W^C \gg Q$

This case would be realized if CH_4 were nearly of the ionic structure $C^{4-}(H_4)^{4+}$, for it requires that the difference between the electron affinities of the C and H attracting centers (appropriately screened) be large compared to the various integrals (3), notably the resonance terms Q, R which are the main cause of the molecular binding. It further requires $W^H - W^C \gg Q$ so that electrons are in the mean attracted from H to C rather than *vice versa*. Actually this case will be a rather poor approximation in CH_4, for the ionization potentials of C and H are nearly equal, and their electron affinities small. Nevertheless it is instructive to carry through a calculation for this case, because it is desirable to solve the secular determinant (4) for as many different limiting cases as possible, and especially because it here proves possible to obtain simple and illuminating formulas for the energy with arbitrary arrangement of the H atoms.

The mathematical simplicity of the present case rests in our ability to use a series development in the ratios of the integrals (3) to $W^H - W^C$. It is convenient to introduce a parameter λ into Eq. (4) by the following scheme: *multiply each Q or T term in* (5) *by* λ, *and each C or D term by* λ^2. The series development may then be regarded as a power series in λ. The convergence of the development is, of course, due to the smallness of the expressions (3) rather than of λ, since finally one must set $\lambda=1$. The rôle of λ is thus only a formal one, and is primarily to describe the degree of approximation which first yields the tetrahedral model. The calculation will yield the following interesting result: the molecule's energy is a series in even powers of λ and is independent of the way the H atoms are arranged if the development is carried only to terms in λ^2 inclusive, but is a minimum for the tetrahedral model when terms of order λ^4 are included. These λ^4 terms are of two types. One kind arises from fourth powers of Q, T; the other involves the product of a first power of C, D

[4] In using (6) it must be mentioned that to specify a real π wave function completely, it is necessary to specify the phase ϵ in its azimuthal factor $\cos(\varphi-\epsilon)$. In (6) the value of ϵ is zero if the apse line for measuring φ is taken in the plane $x-\mathrm{C}-i$. In calculating the values of the elements r in (4), use must be made of the fact that if ψ_π, ψ_π' denote π wave functions of C with different phases,

$$\int\int\int \psi_\pi\psi_\pi' V_{H_i}dv = -C_\pi\cos(\epsilon-\epsilon').$$

and a squared term in Q, T. (Squared terms in C, D prove to be absent.) Both types need not be of coordinate importance, but fortunately both yield the same dependence of energy on angular arrangement, favoring the tetrahedron. It appears impossible to say which type is the more important, as an answer to this question would require knowledge of the magnitude of C, D compared to Q. One knows, to be sure, that Q is large compared to C, D, but this is insufficient.

We now proceed with the details of the calculation. The first step is to apply a transformation which will for our purposes reduce the eighth order secular determinant to a fourth order one. The transformation in question is

$$S(ij) = -S(ji) = -K(ij)/h\nu(ij), \qquad S(ii') = \delta_{i,i'}, \qquad S(jj') = \delta_{j,j'} \tag{8}$$

where δ is the usual Kronecker symbol and the $K(mn)$ are defined by writing the matrix elements of (4) as $K(mn) - W\delta_n{}^m$. Note that because of the T terms in (5) the $K(mn)$ involve W. The indices i, i' refer to any of the C levels and j, j' to any of the H ones (i.e., the ground states of any of the four H atoms). One can verify that in the transformed matrix $S^{-1}KS$ the elements ij (which replace a, b, c, d, q in (4)) are of the order λ^3 and so affect the four lowest, i.e., perturbed carbon, roots of (4) only in the approximation λ^6. As we shall stop with λ^4, we therefore need retain in this transformed matrix only the fourth order piece (ii') which embraces the four C roots. On calculating[5] this piece by means of (8) one finds that it gives the secular equation

$$|L(ii') - \delta_{i,i'}W| = 0 \tag{9}$$

with

$$L(ii) = K(ii) + \sum_j \frac{K(ij)^2}{h\nu(ij)} - \left\{ \sum_{i',j} \frac{K(ij)K(ji')K(i'i)}{h\nu(ij)h\nu(i'j)} + \sum_{j,i',j'} \frac{K(ij)K(ji')K(i'j')K(j'i)}{h\nu(ij)h\nu(i'j)h\nu(ij')} \right\} \tag{10}$$

$$L(ii') = K(ii') + \sum_j \frac{K(ij)K(ji')}{h\nu(i'j)}. \tag{11}$$

The terms in braces are of degree λ^4; the others of degree λ^2 or lower. We have carried the expressions for the L's far enough to give the expansion of (9) to λ^4. This means that it has only been necessary to carry the off-diagonal elements (11) to the approximation λ^2. If we were interested in individual roots of (9), instead of merely the sum, we would need to carry these elements to the approximation λ^4, since to determine individual roots of (9) to λ^4 one would need to know the coefficients of W^2, W, W^0 to λ^8, λ^{12}, λ^{16}, respectively, whereas we are interested purely in the coefficients of W^3, W^4. In virtue of (10), (11), (5), to our approximation the explicit form of (9) is

$$\begin{vmatrix} H_s + I_s\sum_i\sum_j(\mathbf{i}\cdot\mathbf{j}) - W & M_s\sum l_i & M_s\sum m_i & M_s\sum n_i \\ M_p\sum l_i & f(l) - W & J\sum l_i m_i & J\sum l_i n_i \\ M_p\sum m_i & J\sum l_i m_i & f(m) - W & J\sum m_i n_i \\ M_p\sum n_i & J\sum l_i n_i & J\sum m_i n_i & f(n) - W \end{vmatrix} = 0 \tag{12}$$

with

$$\left.\begin{aligned} f(q) &= W_p{}^C - 4\lambda^2 C_\pi + J\sum_i q_i{}^2 + \sum_i\sum_j q_i q_j[I_p + N(\mathbf{i}\cdot\mathbf{j})] \\ H_s &= W_s{}^C - 4\lambda^2 C_s - 4\lambda^2\tau_s Q_s{}'^2 + 4\lambda^4\tau_s{}^3 Q_s{}'^4, \quad J = \lambda^2(C_\pi - C_\sigma) - \lambda^2\tau_p Q_\sigma{}'^2 \\ I_k &= \lambda^4\tau_s\tau_p D Q_s' Q_\sigma' + \lambda^4\tau_s\tau_p\tau_k Q_\sigma{}'^2 Q_s{}'^2, \quad M_k = -\lambda^2 D - \lambda^2\tau_k Q_s' Q_\sigma' \\ N &= \lambda^4\tau_p{}^2 Q_\sigma{}'^2(C_\sigma - C_\pi) + \lambda^4\tau_p{}^3 Q_\sigma{}'^4 \end{aligned}\right\} \tag{13}$$

[5] The matrix elements of S^{-1} needed for computing $S^{-1}KS$ are found by noting that (8) gives nearly a unit matrix, so that

$$S^{-1} = 1 - (S-1) + (S-1)^2 - (S-1)^3 + \cdots.$$

where the i and j summations each embrace a, b, c, d and where

$$1/\tau_k = W^H + B - W_k{}^C > 0, \quad (k = s \text{ or } p); \qquad Q_k' = Q_k + T_k(W_k{}^C - W), \quad (k = s \text{ or } \sigma) \tag{14}$$

$$(\mathbf{i}\cdot\mathbf{j}) = l_i l_j + m_i m_j + n_i n_j = \cos(\mathrm{C-H}_i, \mathrm{C-H}_j), \qquad (i, j = a, b, c, d). \tag{15}$$

We have treated B as part of the H atoms' unperturbed energy in defining the τ_k or $1/h\nu(ij)$. This avoids the necessity of treating the B terms as perturbations. The rôle of the B terms is thus a trivial one, without appreciable influence on the properties of directional valence. When one drops terms beyond λ^4, the expansion of (12) is of the form

$$(W - W_p{}^C)^3(W - W_s{}^C) + \lambda^2(a_5 W^5 + a_4 W^4 + \cdots + a_0) + \lambda^4(b_7 W^7 + \cdots + b_0) = 0. \tag{16}$$

The coefficients a of the λ^2 terms are easily seen to be independent of the molecular arrangement since the sum of the squares of three direction cosines is unity. The terms proportional to W^5, W^6, W^7 exist because the second relation of (14) makes the elements (13) nonlinear in W. The fact that (16) is a seventh degree expression in W gives the superficial appearance of a seventh degree secular problem, but this is only an illusion, for it is only legitimate to take the four roots which reduce to C levels at infinite C−H separations. The other three roots are devoid of any significance, as nearness to C levels was assumed in reducing the determinant to the fourth order. The occurrence of higher powers than W^4 in (16) may be obviated by depressing the higher powers of W by the approximate relation

$$W^4 = 6w^2W^2 - 8w^3W + 3w^4 + \lambda^2[(6a_5w^2 + a_3)W^3 + (-8a_5w^3 + 6a_4w^2 + a_2)W^2 + \cdots]$$

obtained by solving (16) first with $\lambda = 0$ and then correcting to λ^2 inclusive. Here for simplicity we have assumed the origin for the energy so chosen that the mean root is zero when $\lambda = 0$, i.e., that $W_s{}^C = -3w$, $W_p{}^C = w$ where $4w$ is the carbon s-p separation. This assumption involves no loss of generality and simplifies the calculations materially. Thus (16) is transformed into a fourth degree equation $AW^4 + BW^3 + \cdots = 0$. The sum X of the four relevant roots is thus,

$$X = -\frac{B}{A} = -\frac{\lambda^2[a_3 + 6a_5w^2] + \lambda^4[b_3 + a_3a_4 + a_2a_5 + w^2(6b_5 + 12a_4a_5) - 8w^3(b_6 + a_5^2) + 39b_7w^4] + \cdots}{1 + \lambda^2 a_4 + \cdots}. \tag{17}$$

It will be noted that the absence of orthogonality makes the procedure somewhat more complicated than it would otherwise be. If we were willing to assume perfect orthogonality and so set $T = 0$ in (5) there would be no terms higher than W^4 in (9) or (16) and one could use the usual spur relation $X = -\sum L(ii)$ which actually is invalidated by the non-orthogonality. It is clearly to be understood that the spur in question is that of (9) or (16) and not that of (4), since we are interested in the sum of only half the roots of (4). It does not appear a legitimate approximation to assume orthogonality as (7) shows that T is of the same order of magnitude as $Q/h\nu(\mathrm{C;H})$ unless fortuitously Q and R are very nearly equal. Although the non-orthogonality invalidates the ordinary spur relation, it is still very much easier to calculate the sum than individual roots, as the latter would require solution of a biquadratic equation, which we have avoided.

When the explicit values of the coefficients in (16) are calculated by means of (14–15) it is found that (17) becomes

$$X = \alpha + \beta\mathbf{p}^2 + \gamma\textstyle\sum_i\sum_j(\mathbf{i}\cdot\mathbf{j})^2, \tag{18}$$

where α, β, γ are independent of the arrangement of the H atoms, $(\mathbf{i}\cdot\mathbf{j})$ is defined as in (15), and $\mathbf{p}$ is a vector of components $\sum l_i$, $\sum m_i$, $\sum n_i$. This vector is clearly proportional to the electric moment of the molecule. It is particularly noteworthy that to our degree of approximation λ^4, the dependence of X on the molecular arrangement, i.e., on l_1, l_2, $\cdots$ n_4, is only through the two combinations $\sum\sum(\mathbf{i}\cdot\mathbf{j})^2$ and $\mathbf{p}^2$. The coefficients in (18) have the following values in terms of the integrals (3)

$$\beta/\lambda^4=2\tau_s\tau_p D[Q_\sigma Q_s+2(T_sQ_\sigma-Q_sT_\sigma)w]+\tau_s^2\tau_pQ_s^2(Q_\sigma-4T_\sigma w)^2+\tau_p^2\tau_sQ_\sigma^2(Q_s+4T_sw)^2$$
$$+D(\tau_s+\tau_p)(Q_sT_\sigma+T_sQ_\sigma)+\tau_s\tau_p[2Q_\sigma T_\sigma Q_s^2+2Q_sT_sQ_\sigma^2+4(Q_\sigma^2T_s^2-Q_s^2T_\sigma^2)w], \quad (19)$$

$$\gamma/\lambda^4=\tfrac{1}{2}\tau_p^2(C_\sigma-C_\pi)Q_\sigma^2+\tfrac{1}{2}\tau_p^3Q_\sigma^4+2\tau_p(C_\sigma-C_\pi)T_\sigma Q_\sigma+2\tau_p^2Q_\sigma^3T_\sigma \quad (20)$$

with τ as in (14). The corresponding formula for α could be given, but is of no interest.

The all important question is now the signs of β and γ. These are both positive because of the following considerations. We have already mentioned after Eq. (3) that the C, D, Q, T may all be considered positive, and τ is positive in virtue of (14). Furthermore $C_\sigma-C_\pi$ is positive since the σ_i wave function overlaps the hydrogen atom H_i much more than do the π_i functions. Hence every term in (20) is positive. Eq. (19) contains two negative terms, but these are of subordinate importance for the following reasons. In the first place, the carbon s-p separation $4w$ may be small compared to the separation τ between the H and C levels. If this is the case Tw will be small compared to Q, since (7) shows that T is of the order of magnitude Q/τ inasmuch as Q and R are usually very roughly of the same order. Furthermore, even if the s-p interval should be so large that Tw and Q are of the same order of magnitude, there are so many positive terms that it would be only with a very curious and unreasonable collection of values for the integrals (3) that the negative terms could predominate. In particular, if the s and p bonds are nearly equal, the value of T_sQ_s will not differ greatly from that of T_sQ_σ, so that the factors $(T_sQ_\sigma-Q_sT_\sigma)$ and $(Q_\sigma^2T_s^2-Q_s^2T_\sigma^2)$ are comparatively small.

The most stable molecular arrangement is that which minimizes (18), since $2X$ is the binding energy. A convenient alternative way of writing (18) is

$$X=\alpha+(16/3)\,\gamma+(\beta-\tfrac{2}{3}\gamma)\mathbf{p}^2$$
$$+2\gamma\textstyle\sum_{i,\ j\ (j>i)}[(\mathbf{i}\cdot\mathbf{j})+\tfrac{1}{3}]^2. \quad (21)$$

Eqs. (18) and (21) are identical inasmuch as $\mathbf{p}=\sum\mathbf{i}$, $\mathbf{i}\cdot\mathbf{i}=1$, and as the sum in (18) included $j\leqq i$ in addition to $j>i$. Now the tetrahedral model alone possesses *both* of the two following properties: (a) absence of an electric moment $\mathbf{p}$; (b) a common value $-\frac{1}{3}$ for every term of the form $\mathbf{i}\cdot\mathbf{j}(i\neq j)$. (The easiest way to see that the tetrahedron fulfills (b) is to note that the projections on $C-H_a$ of unit vectors directed along $C-H_b$, $C-H_c$, $C-H_d$ are all equal, and of magnitude $-\frac{1}{3}$ because of the absence of an electric moment). Eq. (21) shows immediately that the tetrahedral model possesses the least energy of all models if $\beta\geqq\frac{2}{3}\gamma$. It is not unlikely that the latter inequality is fulfilled. For instance, if we suppose that the Q,T are more important than the C, D terms, that Tw/Q is small, that $\tau_s=\tau_p$ and that the s and p bonds are of equal intensity (i.e., $Q_\sigma=Q_s$, $T_\sigma=T_s$), Eqs. (19–20) show that $\frac{2}{3}\gamma$ is between one-sixth and one-third as large as β; actually the s bonds are weaker than the p, but perhaps not enough to make $\frac{2}{3}\gamma>\beta$.

One can also see beyond all reasonable doubt from (18) or (21) that the tetrahedral model is superior even if $\beta<\frac{2}{3}\gamma$. It is an immediate consequence of (21) that the tetrahedron has the least energy of all models devoid of an electric moment, since with $\mathbf{p}=0$ the question of the sign of $\beta-\frac{2}{3}\gamma$ does not enter. Among the models with an electric moment, the only arrangement that seems at all probable is a pyramidal model with the C atom at its apex and the four H atoms at the corners of a square base. One easily finds that in this model the sum $\sum(\mathbf{i}\cdot\mathbf{j})^2$ has its minimum value when each $C-H$ axis is inclined at $\cos^{-1}3^{-\frac{1}{2}}=54.7°$ to the axis of the pyramid. Then some of the $(\mathbf{i}\cdot\mathbf{j})$ $(i\neq j)$ have the value $+\frac{1}{3}$, the rest the value $-\frac{1}{3}$. The 54.7° pyramid thus gives the same value for the third term of (18) as the tetrahedron, but the pyramid has an electric moment and so gives a larger value of the second term. Of course this still does not disprove the possibility of some freak, unsymmetrical model with an electric moment, but we must not forget the physical fact that dielectric constant data unquestionably reveal that CH_4 has no moment. Irrespective of this fact, one can progress a step further towards complete mathematical rigor by noting that the tetrahedral model, regardless of the

sign of $\beta-\frac{2}{3}\gamma$, fulfills the analytical criterion

$$\sum_i[\mathbf{i}\times\mathbf{j}](\mathbf{i}\cdot\mathbf{j})=0 \qquad (22)$$

that $\sum_{ij}(\mathbf{i}\cdot\mathbf{j})^2$ be an extremum. That (22) is the condition for the minimum of this sum can be verified by writing the sum explicitly in terms of the l's, m's, and n's, and then differentiating with respect to, say, the m's after the n's have been eliminated by the relations $l_i^2+m_i^2+n_i^2=1$. Satisfaction of (22) by the tetrahedron shows that it is stable with respect to adjacent arrangements, but this does not say that there are not radically different arrangements also satisfying (22) and conceivably giving still lower energy if there is an electric moment. The 54.7° pyramid, the square coplanar model, and collinear arrangements $\mathbf{i}\cdot\mathbf{j}=\pm1$ are all solutions of (22), but each gives a higher value of (18) than the tetrahedron.

Case $W^C-W^H\gg Q$. This is another limiting ionic case, differing from the preceding in that the drift of electronic charge is from C to H rather than from H to C, making the model nearly $C^{4+}(H_4)^{4-}$. This case can be treated by the same kind of perturbation development as the preceding one, but we shall omit the calculations. Without appreciable computation, one can show that the tetrahedral model has the least energy if one neglects the corrections for non-orthogonality, so that one can use the spur theorem.[6] Of course the corrections are important, but in the preceding case, at least, they reinforced rather than counteracted the other terms.

3. Another Method of Approximation with the Hund-Mulliken Method

When Q is of the same order of magnitude as, or larger than, the separation W^H-W^C between the C and H levels, the molecule is no longer usually highly polar, and it is naturally no longer legitimate to use the perturbation developments employed in Section 2. Because of this difficulty it appears no longer possible to find the binding energy for arbitrary arrangements. Instead it is necessary to restrict our attention to models with some degree of symmetry so as to permit factorization of the secular determinant (4). Fortunately the symmetrical models are, of course, the most likely. Three types of symmetrical models will be described and calculated below under (*a*), (*b*), (*c*), and it will be shown that of these the tetrahedron is the most stable. Even with the symmetrical types the calculation is too complicated to be tractable[7] without the following three simplifications: (I) neglect of the *s-p* separation in carbon; (II) neglect of the C and D terms in (4–5); (III) neglect of terms arising from want of orthogonality (the T terms in 4–5).

Assumption (I), *viz.*, that $W_p{}^C-W_s{}^C$ is very small compared to Q, means conditions such that *s-p* hybridization would be a good approximation were the calculation to be made by the Heitler-London method. It is not necessary to make the more stringent restriction that $|W^H-W^C|\ll Q$, as the latter proves to permit little additional simplification beyond that arising from $W_p{}^C=W_s{}^C=W^C$. We can clearly suppose that W^H-W^C is at most of the order Q, since if $W^H-W^C\gg Q$ we would merely revert to the case already covered by perturbation theory. In consequence of this fact, we shall show in the next paragraph that (II) and (III) are good approximations if (I) is granted.

Assumption (II) means that the molecular bonds are supposed to arise mainly from the Hund resonance (our Q) terms rather than from penetration (our C, D) terms. In the preceding cases

[6] If we set $T=0$, the root sum Y which interests us when $W^C-W^H>>Q$ is $Z-X$ where Z is the spur of the complete matrix (4) and X is our previous root sum. The value of Z is independent of the angles, and hence Y has an extremum when X does. When $W^C-W^H>>Q$ the tetrahedral arrangements gives a minimum of $Z-X$ and a maximum of X rather than the reverse as previously. This is because sign changes in τ and in certain of the integrals (3), occasioned by the electronic drift being from C to H rather than from H to C, make the expressions β, γ defined in (19, 20) become negative.

[7] For the regular tetrahedron, which is a special case of the models of class (a) or (c), and which has the most symmetry of all, none of the approximations (I), (II), (III) are necessary, and an exact expression can be derived for the energy, which was given in Eq. (4), Part I. The constants employed in Part I have the following significance in terms of the integrals (3), etc.

$a+3b=4C_s+W_s{}^C$, $\quad a-b=\frac{1}{3}C_\sigma+\frac{8}{3}C_\pi+W_p{}^C$,
$c+3e=2(-Q_s+T_sW_s{}^C)$, $\quad c-e=-(\frac{4}{3})^{\frac{1}{2}}(Q_\sigma-T_\sigma W_p{}^C)$,
$d+3f=-2T_s$, $\quad d-f=-(\frac{4}{3})^{\frac{1}{2}}T_\sigma$, $g\sim0$, $h\sim0$, $\quad k=W^H+B$.

we stated that it was not allowable to forget the C, D terms, even though $C, D \ll Q$, inasmuch as they affected the dependence of energy on arrangement in the approximation CQ^2, DQ^2, whereas Q alone appeared only in the fourth order (cf. Eqs. (19–20)). In the present case, however, the development in ascending powers of $Q/h\nu(\mathrm{H;C})$ is no longer used and in consequence the Q terms will influence the energy of spatial arrangement in the first rather than fourth approximation, thus surely becoming more important than the C terms. This can be seen concretely from later specific energy formulas; the situation is roughly similar to that of an expression like $(a^2+b^2\cos^2\theta)^{\frac{1}{2}}+(a^2+b^2\sin^2\theta)^{\frac{1}{2}}$, which depends on angle in the approximation b^4/a^3 if $b^2 \ll a^2$, but in terms of the order b otherwise. Likewise neglect of orthogonality is a much better approximation than when $W^H - W^C \gg Q$. This can be seen from dimensional considerations. The expressions T_σ, T_π are dimensionless and small compared to unity, while Q has the dimensions of energy. Terms of the form $Q^x(W^H - W^C)^y T^y$ can thus appear along with those of the form Q^{x+y} and could be coordinate in importance with the latter in the previous cases where $|W^H - W^C| > Q$ but not in the present one, where $W^H - W^C$ is at most comparable with Q.

(a) One type of model which is readily treated and which we shall call class (a) is obtained by the following scheme. Let the coordinates of the C atom be 0, 0, 0 and those of the four other atoms be $x, 0, z$; $-x, 0, z$; $0, y', z'$; $0, -y', z'$; Let $\omega = \tan^{-1} z/x$ and $\omega' = \tan^{-1} z'/y'$. This class includes the regular tetrahedron as the special case $\omega = -\omega' = \tan^{-1} 2^{-\frac{1}{2}} = 35.3°$ and the Guillemin-Henri pyramidal model (H atoms at corners of square base, C at vertex) as the special case $\omega = \omega'$, $z = z'$. In order to make our calculations applicable to molecules of the form CH_2X_2 as well as just CH_4, we shall

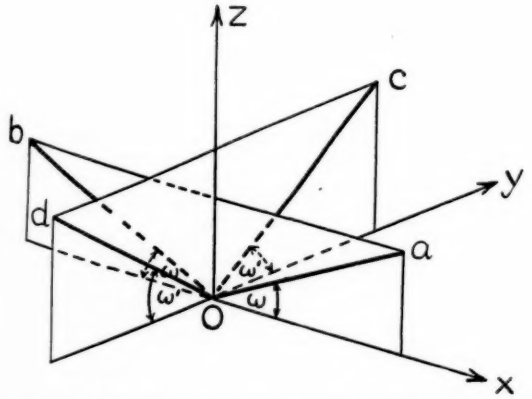

FIG. 1 (class (a)). For CH_4 or CH_2X_2. Here $Oa = Ob$; $Oc = Od$, with H atoms at c, d and a C atom at O. The atoms at a, b are either both H or both X. The regular tetrahedron is the special case $\omega = -\omega' = \tan^{-1} 2^{-\frac{1}{2}} = 35.3°$. In the text the notation $\mathfrak{N}$ or P is used for integrals involving either a or b; and N or Q for those involving c or d.

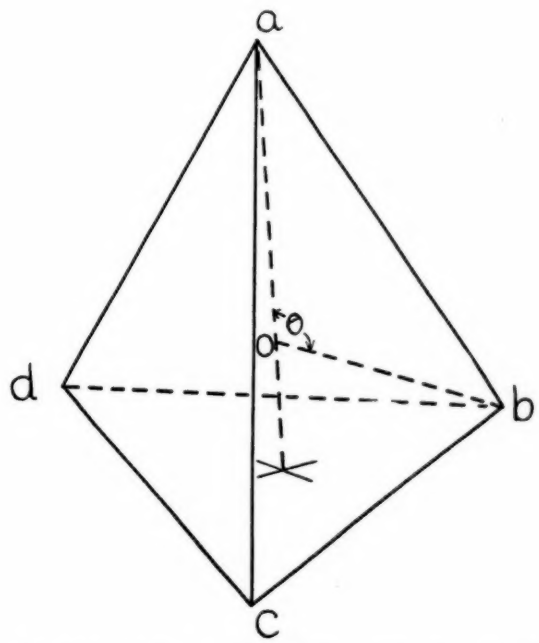

FIG. 2 (class (c)). For CH_4, CH_3X, or NH_3. Here $Ob = Oc = Od$ and $ab = ac = ad$ with H atoms at b, c, d; a C (or N) atom at O and an H or X (or no) atom at a. The z axis is directed along Oa and the xz plane contains aOb. The regular tetrahedron is the special case $\theta = \cos^{-1} -\frac{1}{3} = 109.5°$. The integrals $\mathfrak{N}$ or P apply to a; and N or Q to b, c, d.

not assume that the atoms in the xz plane are the same as those in the yz plane.[8] It will not be necessary to suppose[9] $x^2+z^2=y'^2+z'^2$, i.e., that the two kinds of atoms are equidistant from the C atom, but unfortunately it must be assumed for tractability that they all have the same energy W^H. The resonance integrals between the C atom and the atoms in the xz plane will be denoted by the letter P rather than Q in order to exhibit the fact that they are held by bonds of different intensity than those in the yz plane. It is convenient to choose the eight wave functions as follows

$$\begin{gathered}[\psi(2s),\ \tfrac{1}{2}(\psi_a+\psi_b+\psi_c+\psi_d),\ \psi(2\sigma_z),\ \tfrac{1}{2}(\psi_a+\psi_b-\psi_c-\psi_d)],\\ [\psi(2\sigma_x),\ 2^{-\frac{1}{2}}(\psi_a-\psi_b)],\qquad [\psi(2\sigma_y),\ 2^{-\frac{1}{2}}(\psi_c-\psi_d)].\end{gathered}\tag{23}$$

with notation as in Eq. (1) except for obvious contractions. The secular determinant, originally of degree 8 (cf. Eq. (4)) then factors into a biquadratic and two quadratics. The biquadratic is a quadratic in $(W-W^H)(W-W^C)$ and so easily soluble. Wave functions bracketed together belong to the same factor. The factorization is readily verified and explicit form of the factorized determinants constructed from the transformation property (6) of the carbon p wave functions under rotation. Four of the roots are as follows:

$$W_1=F(P_\sigma^2\cos^2\omega),\qquad W_2=F(Q_\sigma^2\cos^2\omega'),\tag{24}$$

$$W_\pm=G_\pm(P_\sigma^2\sin^2\omega+Q_\sigma^2\sin^2\omega'+P_\pi^2+Q_\pi^2;\ 2P_\sigma Q_\pi\sin\omega-2P_\pi Q_\sigma\sin\omega'),\tag{25}$$

where
$$\begin{aligned}F(a)&=\tfrac{1}{2}(W^H+W^C)-\tfrac{1}{2}\sqrt{[(W^H-W^C)^2+8a]},\\ G_\pm(b;c)&=\tfrac{1}{2}(W^H+W^C)-\tfrac{1}{2}\sqrt{[(W^H-W^C)^2+4b\pm4(b^2-c^2)^{\frac{1}{2}}]}.\end{aligned}\tag{26}$$

The radical sign is used throughout to denote the positive square root. The other four roots are similar except that the factor before the radical sign is $+\frac{1}{2}$ rather than $-\frac{1}{2}$. These other roots are "anti-bonding," i.e., give higher energy than the lesser of the two quantities W^H, W^C, and hence are of no interest to us. The Pauli principle allows two electrons to each bonding root, and so the molecule's energy is

$$2X=2(W_1+W_2+W_+ +W_-).\tag{27}$$

We first note that for given absolute values of ω, ω', and nonvanishing P, Q, the expression (27) has a lower value when ω and ω' have opposite rather than similar signs. This follows from (24–26) and the inequality

$$G_+(b;c')+G_-(b;c')<G_+(b;c)+G_-(b;c)\quad(b\geqq c'>c>0).$$

Hence for any molecule of the type CH_4 or CH_2X_2 the pyramidal model is never that of least energy.

Now let us make the specialization $Q=P$ appropriate to CH_4 if all four H atoms are equidistant from C, and plot (27) as a function of the variables ω, ω'. The value of (27) is then symmetric with respect to the line $\omega=-\omega'$ in the ω, ω' plane, as well as with respect to $\omega=\omega'$. Hence if we consider the behavior of (27) along any curve in the ω, ω' plane, (27) will have extremums where the curve crosses either of these lines. Furthermore, an extremum of (27) along the line $\omega=-\omega'$ occurs at $\omega=\tan^{-1}2^{-\frac{1}{2}}$, as can be verified by differentiation of (27) with respect to ω after first setting $\omega'=-\omega$. Hence the regular tetrahedron gives an extremum of the energy, which closer examination shows

[8] Most commonly the atoms X will be halides, in which case they will be in ^2P rather than in ^2S states like hydrogen. Despite this difference, the analysis is still applicable if we suppose that in the halide's incomplete shell $ms^2\,mp\pi^4\,mp\sigma$, the axis of $mp\sigma$ is directed towards the central atom C and if we neglect the bonding power of ms and $mp\pi$. Such a choice of the axis of $mp\sigma$ is clearly demanded for overlapping favorable to bonding. With these assumptions, only the $2p\sigma$ electron of the halide is involved in the secular problem (4), and the integrals (3) obviously are to be calculated for an $mp\sigma$ rather than $1s$ state of X. Also no harm is done if the letter H similarly symbolize some atom other than hydrogen and not necessarily in an S state. Thus the conclusions of our calculations also apply to compounds such as CCl_4, CCl_2Br_2, CCl_3Br, as well as CH_4, CH_2X_2, CH_3X.

[9] The assumption $x^2+z^2=x'^2+z'^2$ is, however, always needed for the simplification $P=Q$ which we make in connection with CH_4.

to be a minimum rather than maximum. The tetrahedral model is thus stable with respect to adjacent models. This is not quite the same as demonstrating rigorously that it has the least energy of all models of the class, as conceivably there might be a lower minimum at some other values of ω, ω'. Because of algebraic difficulties, it would be difficult to solve the equations $\partial X/\partial\omega = \partial X/\partial\omega' = 0$ explicitly for ω, ω', but rough inspection of the behavior of (27) for various values of the arguments shows that the occurrence of a lower minimum is exceedingly unlikely. In fact the only other minimum appears to be the 54.7° pyramid ($\omega = \omega' = 35.3°$), which is a minimum along the line $\omega = \omega'$, but is a higher minimum because of the considerations in the preceding paragraph. It is interesting to note that this pyramid and the tetrahedron are minima for all values of the relative intensity Q_s/Q_σ of the s and p bonds, including $Q_s/Q_\sigma = 0$ and excluding only the trivial case $Q_s/Q_\sigma = \infty$ where there is no directional valence. The existence of a nonvanishing Q_s is necessary only to make the two minima unequal, as the signs of ω, ω' are immaterial in (24–25–26) if $Q_s = P_s = 0$. Hence just as in Section 2 the tetrahedron takes precedence over the 54.7° pyramid only because of the interplay between the s and p bonds.

(b) **Plane models.** Consider a plane model formed by placing the C atom at the center of a parallelogram, an atom X at each of two opposite corners, and an atom H at each of the two other corners. In this type of model the energy obviously has the same value when the angle α between the diagonals of the parallelogram has the value α as when it has the value $\pi - \alpha$. Hence $\alpha = \pi/2$ gives an extremum, easily seen to be a minimum. With such a value of α, this plane model is merely the special case $\omega = \omega' = 0$ of the models of class (a) and hence has higher energy than the tetrahedron.

Another readily soluble model in which all atoms are in the same plane is that in which the X atoms are at the upper corners, the H atoms at the lower corners, of an isosceles trapezoid, with C on the axis of symmetry. This model is obtainable from class (a) by rotating the plane labelled dOc in Fig. 1 by 90° around the z axis. We can thus take the coordinates of the atoms to be the same as in class (a) except that those of the last two atoms become $x', 0, z'$; $-x', 0, z'$ and $\omega' = \tan^{-1} z'/x'$. The selection of wave functions and factorization are the same as in (23) except that $\psi(2\sigma_y)$ gives an isolated root W^C, while the other three wave functions in the second line of (23) give a cubic of which one root is W^H. Two of the roots are still given by (25) while (24) is replaced by

$$W_1' = F(0), \qquad W_2' = F(P_\sigma^2 \cos^2\omega + Q_\sigma^2 \cos^2\omega'). \tag{28}$$

Using (26) one finds $W_1' + W_2' > W_1 + W_2$, and so the plane model is less firmly bound than the spatial model of the same ω, ω'.

(c) Another tractable case, which we shall call class (c) and which is illustrated in Fig. 2, is that in which the C atom is at the center of a polar coordinate system r, θ, φ while the coordinates of the other four atoms are $r, 0, 0$; $r', \theta, 0$; $r', \theta, \frac{2}{3}\pi$; $r', \theta, \frac{4}{3}\pi$. In order to make our calculations applicable to CH_3X, we shall not necessarily assume that the atom a on the polar (z) axis is identical with the other three atoms held by the C atom, which we may take to be identical H atoms. As before, resonance integrals connected with the C−X bond are denoted by the letter P. Only in the particular case CH_4 shall we suppose $r = r'$. The regular tetrahedron is included as the special case $\theta = \cos^{-1}(-\frac{1}{3}) = 109.5°$. The choice of wave functions and factorization are indicated by the following scheme:

$$\begin{gathered}[\psi(2s),\ \psi(2\sigma_z),\ \psi_a,\ 3^{-\frac{1}{2}}(\psi_b+\psi_c+\psi_d)], \\ [\psi(2\sigma_x),\ (\tfrac{2}{3})^{\frac{1}{2}}(\psi_b-\tfrac{1}{2}\psi_c-\tfrac{1}{2}\psi_d)], \qquad [\psi(2\sigma_y),\ 2^{-\frac{1}{2}}(\psi_c-\psi_d)]\end{gathered} \tag{29}$$

and the bonding roots are

$$W_1 = W_2 = F(\tfrac{3}{4}Q_\sigma^2 \sin^2\theta), \qquad W_\pm = G_\pm(\tfrac{1}{2}P_\sigma^2 + \tfrac{3}{2}Q_\sigma^2\cos^2\theta + \tfrac{1}{2}P_s^2 + \tfrac{3}{2}Q_s^2;\ 3^{\frac{1}{2}}\cos\theta P_s Q_\sigma - 3^{\frac{1}{2}}P_\sigma Q_s) \tag{30}$$

with notation as in (26). One verifies by differentiation with respect to θ, that with (30) and the specialization $P = Q$ appropriate to CH_4, the root sum (27) has a minimum at the tetrahedral angle $\theta = 109.5°$.

4. Case $W^H - W_s^C$ but not $W^H - W_p^C$ Large Compared to Q in Hund-Mulliken Method

This case is a mixture of those in Sections 2 and 3, and is perhaps a better approximation than either to reality since the s-p separation in C is not small, and is probably greater than $W^H - W_p^C$. Here the $2s$ state of C is assumed to lie much deeper than either W^H or the $2p$ states of C. One twice-filled root of the secular determinant is then substantially a carbon $2s$ level; in other words by far the largest coefficient in the corresponding linear combination of wave functions is that of the carbon $2s$ one. If $W^H = W_p^C$, and if we neglect the interaction between s and p bonds, which is small in the present case, the six electrons not absorbed by $2s$ will in the mean be distributed equally between the totality of the four H atoms and the three p levels of C. Thus the $2s$ but not the $2p$ part of the problem will be amenable to the near-ionic approximation and the molecule will be substantially of the structure $C^+(H_4)^-$, except insofar as $W^H \neq W_p^C$. As a first approximation, the bonding effect of the $2s$ wave functions of C can be neglected, since this could be treated by proper adaptation of the "near-ionic" perturbation method of Section 2, and so will give rise only to terms of order $Q^2/h\nu(\mathrm{H};\mathrm{C}_s)$ and higher. Such terms are small compared to the p bonding energies, which are of the order Q. A further, less important effect enhancing the importance of the p as compared to the s bonds is the fact that the $2s$ wave functions represent firmer binding in the C atom and so less "overlapping" of the H atoms than do the $2p$ functions, thus making $Q_s > Q_\sigma$. As a first approximation the bonding action of the $2p$ states may be treated by the method of Section 3 with $Q_s = P_s = 0$. There is now, to be sure, the difference that there are six rather than eight electrons in the secular problem, since two electrons have been absorbed and isolated by the deep $2s$ level. This difference, however, is immaterial inasmuch as in each example of Section 3 one root W_- becomes nonbonding when $Q_s = P_s = 0$, and we have merely to eject $2W_-$, which is now independent of angular arrangements, from the sum (27). The analysis of Section 3 can thus be used and shows that the two most stable models are the regular tetrahedron and the 54.7° pyramid. We saw that with $Q_s = P_s = 0$ these two models were on a par. However, correction for the fact that the s-p interplay (not to mention H-H repulsions) is not completely negligible will make the tetrahedron have the lower energy of the two. This could be demonstrated by introducing the interaction between the s and p bonds as a perturbation of order $Q^2/h\nu(\mathrm{H};\mathrm{C}_s)$ and above. We shall, however, omit the proof, since most readers will probably consider the result sufficiently obvious in view of the fact that the present case is intermediate between the cases of Sections 2 and 3, and in both these cases we showed that the s-p interplay favored the regular tetrahedron over the 54.7° pyramid.

5. Calculation by Heitler-London-Pauling-Slater Method of Electron Pairs

It unfortunately appears impossible without undue labor to make calculations by the Heitler-London method for anything like as great a variety of arrangements as in the preceding Hund-Mulliken procedure. The difficulty with the H-L method is that the secular determinant is of degree 14 and hence is too complicated for explicit solution without either the assumption of electron pairing, wherein the members of a pair have their spins anti-parallel, or else the Heitler-Rumer assumptions to be discussed in Part III. A pair, of course, represents a saturated chemical bond, and the total wave function is invariant when the purely orbital coordinates of the members of a pair are permuted. The qualitative idea of electron pairs as units of chemical structure is due originally to Lewis,[10] who proposed it before the days of quantum mechanics and hence without the wave-mechanical interpretation.

Since the carbon p wave functions are proportional to x, y, z, and so transform like vectors, the most general real linear combination of the carbon s and p wave functions is of the form

[10] G. N. Lewis, *Valence and the Structure of Atoms and Molecules*, Chem. Cat. Co., 1923.

$$\psi_i{}^C = \alpha_i\psi(2s) + \beta_i\psi(2\sigma_i). \tag{31}$$

Clearly the H atom to be paired with this wave function should be located on the axis of quantization $C-i$ of the p term in (31), as then the overlapping is the largest possible. This concept is the basic idea of the Slater-Pauling theory of directed valence. Unfortunately it is impossible to construct four wave functions of the form (31) which are normalized and mutually orthogonal and which project respectively in four *arbitrary* directions $i=a, b, c, d$. This is true since the requirements of normalization and orthogonality yield 10 relations while there are only eight coefficients $\alpha_1, \cdots, \beta_4$ at our disposal. The need of orthogonality is vital, since two electrons with non-orthogonal wave functions have a constraint on the angle between their spins and so are not free to make valence bonds with electrons in other atoms. (The easiest way of seeing this is to pass to the limiting case in which the non-orthogonal functions are identical: the spins associated with the two functions are then anti-parallel and the valences of the two electrons are hence saturated intra-atomically. Abandonment of normalization would not increase the number of allowable directions, as it merely would introduce a trivial constant factor.)

The only models, other than highly unsymmetrical ones, for which it appears possible to construct wave functions with the necessary directive and orthogonality properties are those of class (c), Section 3, for which $\cot^2\theta \leqq \frac{1}{2}$ and those of class (a) for which

$$\cos 2\omega \cos 2\omega' = \sin \omega^2 \sin \omega'^2 \quad \text{with} \quad |\omega'| \leqq \tfrac{1}{2}\pi,\ |\omega| \leqq \tfrac{1}{2}\pi, \qquad \omega'/\omega < 0. \tag{32}$$

The highly unsymmetrical models presumably would be needed for say CWXYZ, but are quite unlikely for CH_4, CH_3X, or CH_2X_2, so that we shall not consider them. For class (c) the proper set of orthogonal functions is

$$\begin{aligned} \psi_a{}^C &= (1-2\cot^2\theta)^{\frac{1}{2}}\psi(2\sigma_a) - 2^{\frac{1}{2}}\cot\theta\,\psi(2s), \\ \psi_j{}^C &= (\tfrac{2}{3}\operatorname{cosec}^2\theta)^{\frac{1}{2}}\psi(2\sigma_j) + (\tfrac{1}{3} - \tfrac{2}{3}\cot^2\theta)^{\frac{1}{2}}\psi(2s) \quad (j=b, c, d), \end{aligned} \tag{33}$$

while for (a)

$$\begin{aligned} \psi_j{}^C &= (1+\cos 2\omega)^{-\frac{1}{2}}[\psi(2\sigma_j) + (\cos 2\omega)^{\frac{1}{2}}\psi(2s)] \quad (j=a, b), \\ \psi_k{}^C &= (1+\cos 2\omega')^{-\frac{1}{2}}[\psi(2\sigma_j) + (\cos 2\omega')^{\frac{1}{2}}\psi(2s)] \quad (j=c, d) \end{aligned} \tag{34}$$

with notation as in Section 3. The orthogonality is readily established with the aid of the relation $\int\int\int \psi(2\sigma_i)\psi(2\sigma_j)dv = \cos(i, j)$ after the cosine is expressed in terms of θ or of ω, ω' with the restriction (32). When $\cos\theta = -\frac{1}{3}$ or $\tan\omega = -\tan\omega' = 2^{-\frac{1}{2}}$ the models reduce to the regular tetrahedron, and then (33) or (34) become the usual Slater-Pauling sp^3 functions.

Because of the inability to find many symmetrical models which permit natural C−H paired bonds, it is in a certain sense impossible to demonstrate in completely quantitative fashion that the tetrahedral model is the most stable in the Heitler-London method. Pauling's criteria of "maximum overlapping," to be sure, make this model very reasonable indeed, as he has shown.[11] Quite irrespective of this fact, the mere inability to "localize" the bonds with symmetrical models other than those cited must be regarded as strong evidence that other models do not fit naturally into the scheme of things and so yield less bonding energy.[12]

[11] L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931).

[12] Essentially this point has also been noted in an interesting paper by R. Hultgren, Phys. Rev. **40**, 891 (1932). His wave functions are more general than ours in that d states are admitted to the linear combinations, but less general in that all the functions are supposed to have the same hybridization ratio. Eqs. (33) and (34) each involve two such ratios. Four would be required for CWXYZ. Presumably the number of different ratios required is the same as the number of different kinds of atoms attached by C. If this is the case then all the C wave functions of CH_4 have the same ratio and the tetrahedral model follows uniquely simply from the requirement of orthogonality. Nevertheless it seems of some interest for us to verify that introduction of two unequal ratios in place of one raises the value of (35) in CH_4.

There is no difficulty in showing that for CH_4 the regular tetrahedron has the least energy of all the models of class (c) with $\cot^2\theta \leqq \frac{1}{2}$ or of class (a) obeying (32). Under the assumption of perfect pairing and neglect of everything but exchange terms the molecular energy is

$$W = \sum_i J_{ii} - \tfrac{1}{2}\sum_{i,\ j(i\neq j)} J_{ij} \quad + \text{constant} \tag{35}$$

where J_{ij} is the exchange integral for the combination $\psi_i{}^H$, $\psi_j{}^C$. Eq. (35) is the embodiment of the well-known results that the exchange energy associated with a saturated bond a, b, is $+J_{ab}$ and that this energy is $-\frac{1}{2}J_{bc}$ between a member b of a pair and any other electron c not its mate in the pair.[13] As usual, we shall neglect all H-H forces or H-H overlapping. By means of the transformation relation (6) it is possible to express (35) in terms of θ or ω, ω' and the essentially diatomic integrals

$$N_{kl} = -\int\int\int\int\int\int \psi_H(1)\psi_k(2)\mathbf{H}\psi_l(1)\psi_H(2)dv_1dv_2 \quad (k, l = 2s,\ 2p\sigma, \text{ or } 2p\pi \text{ of C}). \tag{36}$$

The minus sign has been inserted in order to make most of the N_{kl} positive. Except for sign, the expressions (36) are exchange integrals when $k=l$. The value of $N_{\sigma\pi}$ is zero. It is readily shown, from band spectrum data or by approximate calculation, that $N_{\sigma\sigma}$ and N_{ss} are both positive, while $N_{\pi\pi}$ is negative.[13a]

In the case of (33) we find

$$W = -\tfrac{5}{2}N_{\sigma\sigma} + 4N_{\pi\pi} + \tfrac{1}{2}N_{ss} + 2^{\frac{1}{2}}(1-2\cot^2\theta)^{\frac{1}{2}}(-3\operatorname{cosec}\theta + 3\cot\theta)N_{\sigma s} - (\mathfrak{N}_{\sigma\sigma} - N_{\sigma\sigma})(1-3\cot^2\theta)$$
$$+ (\mathfrak{N}_{ss} - N_{ss})(\tfrac{1}{2} - 3\cot^2\theta) + \mathfrak{N}_{\pi\pi} - N_{\pi\pi} + 2^{\frac{1}{2}}(3\mathfrak{N}_{\sigma s} - 3N_{\sigma s})\cot\theta(1-2\cot^2\theta)^{\frac{1}{2}}. \tag{37}$$

In order to make our calculations adaptable to CH_3X or CHX_3, we have allowed atom a in Fig. 2, Section 3, to be different from the other three atoms b, c, d held by C, and so yield values of the integrals (36) which may be different than those for the other bonds and which are distinguished by being printed in German type. Thus in CH_3X, $\mathfrak{N}$ denotes (36) with subscript X substituted for H, while $\mathfrak{N} = N$ in dealing with CH_4. When one sets $\mathfrak{N} = N$, (37) depends on θ only in the terms proportional to $N_{\sigma s}$, which are peculiar to s-p hybridization. One verifies by differentiation with respect to θ that then if $N_{\sigma s} > 0$, $\mathfrak{N} = N$, Eq. (37) has a minimum at $\cos\theta = -\frac{1}{3}$, giving us the regular tetrahedron. The assumption $N_{\sigma s} > 0$ is correct, for the charge cloud of a $2p\sigma$ wave function is dumb-bell shaped with opposite signs for $\psi(2\sigma)$ on the two ends, so that the sign of $N_{\sigma s}$ is dependent on which end of the dumb-bell one places the H atom. To obtain favorable bonding one must choose the end for which $N_{\sigma s}$ is positive, as is obvious from "overlapping" considerations or from the fact that the minimum of (37) is higher with $N_{\sigma s} < 0$ than with $N_{\sigma s} > 0$. When $\cot^2\theta = \frac{1}{2}$ the three axes C$-b$, C$-c$, C$-d$ are mutually orthogonal; there is then no hybridization and atom a is held only by an s bond; under these conditions it is not necessary to restrict atom a to the axis $\theta = 0$, as it is easily shown that the energy is independent of the alignment of C$-a$ relative to the three orthogonal axes C$-b$, C$-c$, C$-d$.

In the case of models of class (a) with the restriction (32) one finds that (35) becomes

$$W = -\tfrac{5}{2}N_{\sigma\sigma} + 4N_{\pi\pi} + \tfrac{1}{2}N_{ss} + \mathfrak{N}_{\sigma s}g(\omega', \omega) + N_{\sigma s}g(\omega, \omega') + (\mathfrak{N}_{ss} - N_{ss})[1 - 2f(\omega') + f(\omega)]$$
$$+ (\mathfrak{N}_{\sigma\sigma} - N_{\sigma\sigma})[-2f(\omega) + \cos^2 2\omega f(\omega) + 2\sin^2\omega\sin^2\omega' f(\omega')]$$
$$+ (\mathfrak{N}_{\pi\pi} - N_{\pi\pi})[\sin^2 2\omega f(\omega) + 2f(\omega')(1 - \sin^2\omega\sin^2\omega')] \tag{38}$$

with

$$f(\omega) = (1+\cos 2\omega)^{-1},\ g(\omega', \omega) = -2(\cos 2\omega)^{\frac{1}{2}}[1 + f(\omega)] + 4(\cos 2\omega')^{\frac{1}{2}}f(\omega')\sin\omega\sin\omega'.$$

In order to make the calculations applicable to CH_2X_2, we have allowed atoms a and b to be different

[13] Cf. for instance J. C. Slater, Phys. Rev. **34**, 1307 (1929). His K is our J.

[13a] See, for example the table given by Coolidge, Phys. Rev. **42**, 198 (1932).

from c, d, and so give rise to integrals $\mathfrak{N}$ rather than N. As before, when we make the specialization $\mathfrak{N}=N$ appropriate to CH_4, a dependence of W on angle exists only in virtue of the terms involving N_{ss}. That (38) then has an extremum at the tetrahedral configuration is most easily demonstrated by a symmetry argument: *viz.*, when $\mathfrak{N}=N$ the expression (38), regarded as a function of ω, ω', is symmetric about the line $\omega=-\omega'$ in the ω, ω' plane, and so will have an extremum along the curve (32) at the intersection of this curve with this line. The coordinates of the intersection are $\omega=-\omega'=\tan^{-1}2^{-\frac{1}{2}}$, the tetrahedral values.

Slater[14] has remarked that the Heitler-London and Hund-Mulliken methods are equivalent in the last analysis as they reach the same goal when pushed to final accuracy by inclusion of higher approximations (notably addition of polar terms in the H-L and antisymmetrization and inclusion of electron repulsion in the H-M). Of course what Slater says is ultimately true, but when one stops at the first approximation the resemblance between the two methods is very remote in polyatomic molecules. The superiority of the tetrahedron over other molecules which could be calculated was shown above to owe its existence in the H-L-P-S method entirely to the integral N_{ss} which represents the interplay between the s and p bonds and epitomizes the s-p hybridization. On the other hand in the H-M method the p bonds alone were sufficient to insure the superiority of the tetrahedron over all other models with the single exception of the 54.7° pyramid. The tetrahedron was superior to this pyramid because, unlike the latter, the tetrahedron involved no s-p hybridization at all!

6. Configuration of Some Other Molecules, Notably CHX_3, CH_2X_2, CWXYZ, BeX_2, OX_2

The "near-ionic" perturbation calculation given in Section 2 can be extended without particular difficulty to the case in which the central atom is not necessarily carbon, and attaches any number of other atoms, provided only that in all there are precisely eight electrons available for the bonding. There are, of course, in general, plenty of electrons of lower principal quantum number, but these are treated as nonbonding. In place of (18) one finds

$$X=\alpha'+\sum_i\sum_j\beta_{ij}(\mathbf{i}\cdot\mathbf{j})+\sum_i\sum_j\gamma_{ij}(\mathbf{i}\cdot\mathbf{j})^2 \quad (39)$$

where $\mathbf{i}$, $\mathbf{j}$ are unit vectors along the axes C$-i$, C$-j$ and where β_{ij}, γ_{ij} are defined nearly as in (19), (20) except that they are symmetrical in i,j. For instance

$$D^i\tau_s{}^j Q_s{}^j\tau_p{}^j Q_\sigma{}^j+D^j\tau_s{}^i Q_s{}^i\tau_p{}^i Q_\sigma{}^i$$

replaces $2\tau_s\tau_p DQ_sQ_\sigma$ in the first term of (19). Superscripts are, of course, now added to indicate that the integrals (3) have different values for a bond involving atom i than one involving atom j, and instead of (14) one has $1/\tau_k{}^j=W^i+B_j-W_k{}^c$ with W^c, W^i denoting respectively the unperturbed energy of the central atom and that of atom j. Our discussion does not apply to double or multiple bonds, and so we must suppose that atoms i, j, $\cdots$ each have only one solution of Schrödinger's equation which is important for bonding.

Eq. (39) throws considerable light on molecular arrangement. When we remember that the β_{ij} and γ_{ij} are positive and that the terms γ_{ij} are due purely to the bonding by the carbon p wave functions, while the β_{ij} are due to the interplay between the s and p bonding actions (cf. Eqs. (19, 20)), we see that the axes C$-i$, C$-j$ joining any two atoms i,j to the central atom seek to align themselves at right angles to each other if the p wave functions alone are important for bonding. However, if the s-p interplay is appreciable, the angle $i-$C$-j$ will tend to increase towards 180°, as $\mathbf{i}\cdot\mathbf{j}$ has its minimum value at 180° as compared with 90° for $(\mathbf{i}\cdot\mathbf{j})^2(i\neq j)$. Of course it is impossible for all bonds to be mutually at right angles if more than three atoms are attached to the central atom, and in CH_4 the tetrahedral arrangement represents, so to speak, the nearest the bonds can come to such angles. In molecules in which the attached atoms are not all alike, the values of β_{ij}, γ_{ij} will be greater for certain pairs of bonds than for others. These pairs will tend to set themselves at the optimum angles even though this involves making some of the other axes inclined to each other at

[14] J. C. Slater, Phys. Rev. **41**, 255 (1932).

unfavorable angles. For instance, consider a hypothetical ideal case in which γ_{12}, γ_{13}, γ_{23}, γ_{14}, γ_{24} are infinitely large compared with $\gamma_{34}\cdots$ and with any β. Then atoms 1, 2, 3 would be located along three mutually orthogonal axes with origin at the central atom, and atom 4 would be located on the axis C−3 (probably on the opposite side of C from 3) though this leads to the worst possible value of the term involving β_{12}, β_{13}, β_{23}, β_{14}, β_{24}, γ_{34}. In short, the most important pairs of bonds are greedy and tend to assume the most favorable angles at the expense of their fellows. Hence the correct structure when the carbon atom attaches four atoms not all of the same type may be described as a distorted tetrahedron. (Strictly speaking the model is still a tetrahedron, but not a regular one. We insert the adjective "distorted" because we use the word tetrahedron usually only in connection with the regular type.) One can easily see that pyramidal models, where all four attached atoms are on one side of a plane containing the central atom, and plane models will yield higher values of (39) than a properly chosen distorted tetrahedron. Some particular molecules are the following:

CH_2X_2. Here the model will be one of type (a), shown in Fig. 1, Section 3, but with in general $-\omega' \neq \omega \neq \tan^{-1} 2^{-\frac{1}{2}}$ unless the C−H and C−X bonds are very nearly equal. If P_σ is large compared with P_s, Q_σ, and Q_s, the angle ω will be nearly 45° and ω' nearly 0.

CH_3X or CHX_3. The appropriate model is one of type (c), shown in Fig. 2, with the tetrahedral value 109.5° for θ in CH_3X only if $\beta_{HX}=\beta_{HH}$, $\gamma_{HX}=\gamma_{HH}$. If $\gamma_{HH}\gg\gamma_{HX}$ and $\gamma\gg\beta$ then θ will be nearly $\tan^{-1} 2^{-\frac{1}{2}}$, and the three C−H axes will be nearly at right angles. If $\gamma_{HX}\gg\gamma_{HH}$ and $\gamma\gg\beta$ the value of θ will be nearly 90°, and the plane of the three H atoms will almost contain the central atom.

NH_3. For mathematical purposes the ammonia molecule is equivalent to a special case of CH_3X in which atom X is held by a bond of zero intensity (i.e., $\beta_{HX}=\gamma_{HX}=0$) and so is effectively non-existent. As already stated, the fact that the central atom is N rather than C is immaterial for formal considerations so long as there are precisely eight electrons. The value of θ is found by minimization of (39) to be $\cos^{-1}[(\gamma-\beta)/3\gamma]^{\frac{1}{2}}$ if $\beta\leqq\gamma$ and 90° if $\beta\geqq\gamma$. Thus θ is bounded by 54.7° and 90°. If $\beta=0$ is a good approximation, θ will be 54.7° and the three NH axes will be inclined at 90°. If the *s-p* interplay β were the most important thing, which is surely not so, the angle θ would be 90°, and the model would be coplanar. Actually, Lueg and Hedfeld determine θ from band spectra to be 73°, while Dennison and Uhlenbeck find $\theta=68°$ by a different method but likewise based in part on band spectra.[15] Either of these values is within the critical range predicted by the theory.

CWXYZ. Here, naturally, none of the angles should in general be equal.

All the above conclusions are seemingly based on (39) and hence on a "near-ionic" approximation which is not usually an especially close one. To remove this objection we have therefore given another method of approximation for CH_2X_2 and CH_3X (or CHX_3) in Section 3, which applies under different conditions, *viz.*, items (I), (II), (III) of Section 3, and the assumption $W^H=W^X$. These other conditions are more likely to be met when the molecule is primarily nonpolar, and agree with (39) in predicting that the angles cease to be exactly tetrahedral in CH_2X_2 and CH_3X or CHX_3, as (27) ceases to have a minimum at $-\omega'=\omega=\tan^{-1} 2^{-\frac{1}{2}}$ (with Eqs. (24–25)) or at $\cos\theta=-\frac{1}{3}$ (with Eqs. (30)) when $P\neq Q$. The distorted tetrahedra were again found in Section 3 to be better than the corresponding pyramidal and plane models. Similar results can also be obtained with the intermediate method of Section 4, which uses the near-ionic approximation only for the 2*s* part of the problem. The same conclusions thus hold in our three methods of approximation based on the Hund-Mulliken viewpoint. Additional confidence is supplied by the fact that in the Heitler-London-Pauling-Slater method the tetrahedral angles disappear as soon as the calculations are adapted to CH_2X_2, CH_3X or CHX_3, since (37) and (38) cease to have minima at exactly the above values of ϑ or ω, ω' if $\mathfrak{N}\neq N$.

[15] Lueg and Hedfeld, Zeits. f. Physik **75**, 559 (1932); D. M. Dennison and G. E. Uhlenbeck, Phys. Rev. **41**, 313 (1932) or N. Rosen and P. M. Morse, *ibid.* **42**, 210 (1932); these determinations are presumably more accurate than older spectroscopic work which gave values of θ in the neighborhood of 60°.

That the tetrahedral angles are not preserved in CH_2X_2 and CHX_3 is in agreement with x-ray data[16] which reveal the following values for the angles between the two C−Cl axes: $CHCl_3$, 116.4°; CH_2Cl_2, 123.8°, whereas the value disclosed for CCl_4 is 109.5°, exactly the tetrahedral value. The deviations from 109.5° in $CHCl_3$ and CH_2Cl_2 are in the direction to be expected from our theory. Namely, it is known experimentally that C−H bonds (94 kg cal./g mol.) are firmer than C−Cl ones (72 kg cal./g mol.). Hence if the p-bonding effects overshadow the s ones, as they doubtless do, both the H-M and H-L-P-S methods predict that the angles H−C−H and Cl−C−H will become nearer 90° than in the regular tetrahedron, but this entails making the angle Cl−C−Cl greater than 109.5°. It is clear that the deviation should be smaller in $CHCl_3$ than in CH_2Cl_2 since in the latter there are more H−C−H or H−C−Cl angles, causing more overpowering of Cl−C−Cl directional valency. If the latter and s-bonding were negligible, the angle Cl−C−Cl would be 120° in $CHCl_3$ and 180° in CH_2Cl_2.

The same general conclusions on NH_3 as before with (39) are also obtained if one uses the other methods. With the method of Section 3 one minimizes (27) with $P=0$ in (30). The resulting value of θ is given by

$$\cos^2\theta=\tfrac{1}{3}-\tfrac{2}{3}(Q_\sigma^2/Q_\sigma^2) \quad \text{if} \quad Q_\sigma^2\leqq\tfrac{1}{2}Q_\sigma^2 \qquad (40)$$

and $\theta=\pi$ otherwise. The method of Section 4 predicts θ to be slightly greater than $54.7°=\cos^{-1}(\frac{1}{3})^{\frac{1}{2}}$. With the Slater-Pauling method one uses the wave functions (33) but assigns two electrons to ψ_{C_a} since nitrogen has five electrons. The resulting expression for the energy is (37) with $N=0$ but augmented by a contribution

$$\begin{aligned}&\tfrac{3}{2}(1-2\cot^2\theta)\cos^2\theta N_{\sigma\sigma}\\&\quad-3\times2^{\frac{1}{2}}(1-2\cot^2\theta)^{\frac{1}{2}}\cot\theta\cos\theta N_{\sigma s}\\&\quad+2\cot^2\theta N_{ss}+(1-2\cot^2\theta)(W_p-W_s)\end{aligned} \qquad (41)$$

due to the fifth electron. The minimum can only be found numerically, but is located at a somewhat greater angle than 54.7°. The term proportional to W_p-W_s has been inserted in (41) to make some allowance for the influence of the finite s-p separation of the central atom upon the variation of the energy with angle. That the s-p separation does give an angular term is obvious from the fact that with the wave functions now being used, the N atom is in the configuration s^2p^3 at $\theta=54.7°$ and in the configuration sp^4 at $\theta=90°$, so that the internal energy of the N atom is raised in passing from 54.7° to 90°. When we use notation such as sp^4 here we do not mean that individual electrons are of the $2s$ or $2p$ types but that the sum of the squares of the $2s$ and $2p$ parts of the individual functions add to 1 and 4, respectively. The specific form of the term proportional to W_p-W_s in (41) is obtained by examination of the sum of the squares of the $2s$ and $2p$ parts for various angles. The corresponding term was omitted in our formulas (39), (38) for CH_4, CH_2X_2, CH_3X; its inclusion would merely introduce an additive constant W_p-W_s independent of angle, inasmuch as our models of these molecules always involved the aggregate configuration sp^3 whereas the normal state of C is s^2p^2. It must be cautioned that even with such additions we make no allowance for the dependence of the energy of the central atom on L and S in distinction from on the individual l's. The correction for the L, S structure will be studied in Part III.

In the cases of the molecules CH_2X_2, CH_3X, or CHX_3, attempts could be made to calculate quantitatively the deviations of the angles from the tetrahedral values by finding what values of ω, ω' or θ minimize (27), (37), (38), and (39), and so determine the values of the constants (3) or (36) which will yield agreement with experiment. However, this procedure involves algebraic difficulties not encountered in NH_3, where simple formulas for θ were derived, and is promising only in a rough way, since, as in NH_3, the precise minimizing angles will depend on the type of approximation used. For instance, the minimum of (27) with (24–25) does not yield values of ω, ω' conforming to (32). If in particular, as in the method of Section 4, one neglects all s bonding effects by setting $P_s=Q_s=0$ in (24–25) the minimum of (27) is easily found and comes at

$$\begin{aligned}&P_\sigma^2\cos^2\omega=Q_\sigma^2\cos^2\omega'=\tfrac{1}{3}(P_\sigma^2+Q_\sigma^2) && \text{if} && \tfrac{1}{2}\leqq P_\sigma^2/Q_\sigma^2\leqq 2;\\&\omega=45°, && \omega'=0 && \text{if} && P_\sigma^2/Q_\sigma^2\geqq 2;\\&\omega=0, && \omega'=45° && \text{if} && P_\sigma^2/Q_\sigma^2\leqq\tfrac{1}{2}.\end{aligned}$$

This is for CH_2X_2; for CH_3X (Eqs. (30) in (27)) the corresponding values are

$$\begin{aligned}&9Q_\sigma^2\sin^2\theta=6Q_\sigma^2+2P_\sigma^2 && \text{if} && P_\sigma^2/Q_\sigma^2\leqq\tfrac{3}{2};\\&\theta=90° && \text{if} && P_\sigma^2/Q_\sigma^2\geqq\tfrac{3}{2}.\end{aligned}$$

(If instead, (39) is used, the neglect of s bonding means $\beta=0$, and the minimizing angles for CH_3X, for instance, are the same as those just given except that γ_{HX}, γ_{HH} replace P_σ^2, Q_σ^2. If the approximations (I), (II), (III) of Section 3 are made, γ_{HH}/γ_{HX} reduces to Q_σ^2/P_σ^2, as should be.) The fact that $\pi-2\omega=\theta=90°$ if $P^2>>Q^2$ is, of course, an illustration of the tendency of the most important bond angles to become 90° if the p bonding effects predominate.

At this point we may mention a modification which we believe should be made in some of the statements in Pauling's important paper.[11] It conveys the impression that even when there are only two atoms attached the tetrahedral angle 109.5° is the best possible one, whereas we have already intimated that this angle is characteristic

[16] L. Bewilogua, Phys. Zeits. **32**, 265 (1931); P. Debye, Zeits. f. Electrochemie **36**, 612 (1930).

only of four equivalent attached atoms, and that two sole (or the two firmest out of many) attached atoms tend to set their bonding axes at an angle between 90° and 180° whose precise magnitude depends on the relative importance of pure p-bonding and s-p interplay. This can be seen not merely from the near-ionic approximation (39) but also with the two other methods of approximation for the Hund-Mulliken theory given in Sections 3–4, or with the Heitler-London-Pauling-Slater method. The assumptions of Section 4 largely suppress s bonding and so make the valence angle in CX_2 nearly 90°. To calculate this angle with the procedure of Section 3 one has only to set $Q=0$ in (24–25) since CX_2 is formally equivalent to CH_2X_2 with the C−H bonds made infinitely small. The minimum of (27) then comes at $P_\sigma^2\cos 2\omega=P_s^2$ if $P_s\leqq P_\sigma$ and at $2\omega=180°$ if $P_s\geqq P_\sigma$; whether there are four, eight or some intermediate number of electrons is immaterial in this particular case, since two of the roots (24–25) are nonbonding when $Q=0$, making any electrons beyond four superfluous. Similarly in the Heitler-London-Pauling-Slater method, the behavior of CX_2H_2 in the limiting case that the C−H bonds are very weak is given by Eq. (38) if one sets $N=0$ and remembers that ω' is a function of ω given by (36). An explicit formula for the value of the angle $\pi-2\omega$ between the two C−X axes which then minimizes (38) cannot be given because of algebraic difficulties, but the terms of (38) which involve $\mathfrak{N}_{\sigma\sigma}$ have their minimum at $2\omega=90°$ and those which involve $\mathfrak{N}_{\sigma s}$ or $\mathfrak{N}_{ss}$, their minimum at $\omega=0$, making it clear that the minimum will in general come at a value of $\pi-2\omega$ intermediate between 90° and 180° whose precise magnitude depends on the relative sizes of $\mathfrak{N}_{\sigma\sigma}$, $\mathfrak{N}_{\sigma s}$, and $\mathfrak{N}_{ss}$. Terms containing $\mathfrak{N}_{\pi\pi}$ are unimportant because $\mathfrak{N}_{\pi\pi}$ is small. The reason why Pauling appeared to obtain 109.5° quite generally is that he used semiquantitative criteria of "overlapping" rather than the more exact Eq. (35) and assumed a particular value of the relative intensity of the s and p bonds. Of course 109.5° is in the critical range 90°–180°, and may not be far removed from the actual best angle since the p bonding effects favoring 90° are probably the most important factor. In fact, according to Mecke,[17] the actual angle in H_2O is between 103° and 106°.

CX_2, BeX_2, OX_2. We must mention that when the H atoms are completely removed from CH_2X_2, the wave functions appropriate to the third and fourth electrons of C are probably not correctly given by ψ_c^C, ψ_d^C in (34). When the H atoms are missing, these two electrons have no attached atoms with which to be paired, and so need not have equal hybridization ratios as assumed in (34). Also they may even be in the same state, with their spins mutually paired. Another possible choice for the third and fourth wave functions in place of those in (34) is[18]

$$\psi_c'=\psi(2\sigma_y),$$
$$\psi_d'=[k(\omega)]^{\frac{1}{2}}[-\operatorname{cosec}\omega(\cos 2\omega)^{\frac{1}{2}}\psi(2\sigma_z)+\psi(2s)] \quad (42)$$

with $k(\omega)=1/(\operatorname{cosec}^2\omega\cos 2\omega+1)$. Here the y axis has been taken perpendicular to the plane of X−C−X, and the z axis bisects the angle X−C−X. The exchange energy between the third and fourth electrons and the X atoms is minimized by placing both these electrons in the state ψ_c'. The total energy is[19] then

$$W=W'-2\mathfrak{N}_{ss}+2\mathfrak{N}_{\pi\pi}+[1+k(\omega)][W_p-W_s],$$

where W' denotes the value of the expression (38) when one sets $N=0$ and strikes out all terms involving $f(\omega')$ (including those through $g(\omega',\omega)$). More likely, however, the third and fourth electrons both decide to settle in ψ_d', as this makes the carbon configuration nearly s^2p^2 rather than nearly p^4 if 2ω is nearly 90°. The total bonding energy is then

$$W=W'-2\mathfrak{N}_{ss}+[1-k(\omega)][W_p-W_s]$$
$$+2k(\omega)[\cos 2\omega(\mathfrak{N}_{\sigma\sigma}+\cot^2\omega\mathfrak{N}_{\pi\pi})$$
$$-2(\cos 2\omega)^{\frac{1}{2}}\mathfrak{N}_{\sigma s}+\mathfrak{N}_{ss}]. \quad (43)$$

If the third and fourth electrons are entirely missing, as in BeX_2, this energy is $W'-2\mathfrak{N}_{ss}+[1+k(\omega)][W_p-W_s]$. If there are six electrons in the central atom, as in H_2O or OX_2, there are probably two electrons each to the states ψ_c', ψ_d', and the energy is the expression (43) augmented by $2\mathfrak{N}_{\pi\pi}$. In all cases the first two electrons are assigned one each to the first two states of (34). None of these modifications change the critical region in which the best value of the angle X−C−X is located.

The foregoing discussion of CX_2, BeX_2 or OX_2 presupposes the two attached atoms to be identical. Calculations can also be made for the case that they are not equal, but we shall not give them, as they yield nothing qualitatively new regarding the favored angles. When the two attached atoms are not identical and hence not held by bonds of equal strength, one can no longer assume that they are held by pairing with electrons of the central

[17] R. Mecke and W. Baumann, Phys. Zeits. **33**, 833ff. (1932).

[18] It seems quite probable that the functions (42) and first two of (34) are the proper wave functions for C double bonds, rather than the tetrahedral sp^3 functions assumed by Pauling and Slater. At any rate it is certain that the s-p hybridization ratios for double bonds will not be the same as for CH_4. We suggest this combination of (42) with (34) because it gives three directed coplanar valences, *viz.*, those corresponding to ψ_a^C, ψ_b^C, ψ_d'. The C−C bond is here to be located along the z axis, so as to bisect X−C−X. This subject of double bonds will be discussed more fully in a paper by W. G. Penney.

[19] This and shortly following formulas for the bonding energy are obtained by application of (35) and (6), with allowance for the finite s-p separation in the same fashion as in connection with (41). The addition of $-2\mathfrak{N}_{ss}$ and the omission of $f(\omega')$ are consequences of the fact that in (38) those terms containing $\mathfrak{N}_{\sigma\sigma}$, $\mathfrak{N}_{\sigma s}$, $\mathfrak{N}_{\pi\pi}$ which arise from interaction of the third and fourth electrons of C with X_2, are proportional to $f(\omega')$, while the corresponding terms containing $\mathfrak{N}_{ss}$ are proportional to $1-f(\omega')$. Such terms must be dropped and new terms added because of the substitution of new wave functions in place of the third and fourth of (34).

atom which are represented by the first and second wave functions of Eq. (34). Instead the s-p hybridization ratios appropriate to the two bonds may be unequal, whereas (34) assumes equality.

7. Structure of CH_3 and CH_4^+

All of our conclusions concerning the superiority of the tetrahedral or distorted tetrahedral arrangement are contingent upon there being eight electrons available for bonding, so that each of the four lowest roots of the secular Eq. (4) are filled twice. When there are only seven electrons available, as in CH_3 and CH_4^+, the results are sometimes different. In the Hund-Mulliken method they depend upon the particular type of approximation which can be employed, and are as follows.

(i) The near-ionic approximation of Section 2, if allowable, predicts that the most stable models of both CH_3 and CH_4^+ are plane provided the s state of C is beneath the p states by an energy difference large compared to the bonding energy. This can be seen from the following simple argument. In the near-ionic approximation, by far the largest part of the linear combination involved in the wave function is the carbon portion, so that it has a meaning to label the electrons $2s$, $2p$, etc., as in carbon. We showed in Section 2 that the energy of an eight electron system is invariant of the spatial arrangement to the approximation λ^2. The bonding power of any individual electron, however, is of the order λ^2. Hence the arrangements of the H atoms in CH_3 or CH_4^+ which give the lowest energy will be the same as the arrangements of CH_3^- or CH_4 for which one $2p$ electron is removed most easily. The plane models possess this characteristic, since when all the H atoms are in the xy plane, the wave function $\psi(2\sigma_z)$ is nonbonding, except for the small term C_π in (3). Another way of saying the same thing is that with the seven electron configuration $2s^2 2\sigma_x^2 2\sigma_y^2 2\sigma_z$, increased overlapping is secured by placing all the H atoms in the xy plane, whereas this is clearly not true of the more symmetrical, eight-electron configuration $2s^2 2\sigma_x^2 2\sigma_y^2 2\sigma_z^2$.

(ii) The method of approximation of Section 3 is the same for CH_3 as NH_3. The determination of the best value of θ is unaffected by the fact that the energy is now $2W_1+2W_2+2W_++W_-$ instead of the sum (27) appropriate to an eight electron system, for W_- in (30) is a nonbonding root independent of θ, Q when $P=0$. Hence θ is given by (40) and the model is pyramidal if the s bonds are not too intense. On the other hand one finds with this method[20] that CH_4^+ will be plane even if the s bonds are weak unless, also, Q_σ is sufficiently large compared to W^H-W^C.

(iii) With the method of approximation of Section 4, which is near ionic only for the $2s$ electrons, one concludes that the best models of CH_3 and CH_4^+ are respectively models of type (c) with atom a missing and type (a) shown in Figs. 1, 2, Section 3, with the following values of θ or ω, ω'

$$\sin^2\theta=\frac{8}{9}+\frac{1}{18Q_\sigma^2}(W^H-W_p{}^C)^2 \quad \text{if } (W^H-W_p{}^C)^2<2Q_\sigma^2;$$

$$\cos^2\omega=\cos^2\omega'=\frac{8}{9}+\frac{1}{24Q_\sigma^2}(W^H-W_p{}^C)^2 \quad \text{if } (W^H-W_p{}^C)^2<\tfrac{8}{3}Q_\sigma^2;$$

$\theta=\pi$ or $\omega=\omega'=0$ otherwise.

These results are obtained by minimizing[21] $2W_1+2W_2+W_+$ with $P_\sigma=P_s=Q_s=0$ in (30) or with $P_\sigma=Q_\sigma$, $P_s=Q_s=0$ in (24–25). The values $\theta=\pi$, $\omega=\omega'=0$ represent plane models, and so we conclude that the spatial model is obtained by the procedure of Section 4 only if Q is sufficiently large compared with $W^H-W_p{}^C$.

To study CH_3 by the H-L-P-S method one uses the wave functions (33) and sets $\mathfrak{R}=0$ in (37). The minimum of (37) then falls at[22]

$$\cot^2\theta=-\tfrac{1}{4}+\tfrac{3}{4}\frac{(N_{\sigma\sigma}-N_{ss})}{[4N_{\sigma s}^2+(N_{\sigma\sigma}-N_{ss})^2]^{\frac{1}{2}}} \quad \text{if } N_{\sigma\sigma}\geqq N_{ss}+2^{-\frac{1}{2}}N_{\sigma s} \quad (44)$$

[20] For instance when $P=Q$, $\omega=\pm\omega'$, one finds $W_1+2W_2<W_1'+2W_2'$ only if $Q_\sigma^2\cos^2\omega>3(W^H-W^C)^2$. Here W_1, W_2 and W_1', W_2' are levels for certain spatial and plane models as given in (24), (28). The remaining roots (25) are common to both models.

[21] Only five electrons are involved in this sum because two are absorbed by the deep $2s$ states.

[22] Eq. (44) would also give the best value of θ for NH_3 in the H-L-P-S method were it not for the fact that the energy of NH_3 involves the additional terms (41). The term proportional to W_p-W_s in (41) will tend to make θ smaller in NH_3 than in CH_3.

and at $\theta=\pi$ otherwise. Hence this method predicts a pyramidal model only if $N_{\sigma\sigma}$ be sufficiently large compared with N_{ss}, $N_{\sigma s}$. The structure of CH_4^+ cannot be simply studied by the H-L-P-S procedure since no natural scheme of electron pairing is possible.

In view of all the above it is likely that CH_3 has a larger value of θ than does NH_3, and may conceivably even be plane. One thing is particularly clear: there is no reason for CH_4^+ to be a regular tetrahedron like CH_4. Instead CH_4^+ should be a flattened tetrahedron, i.e., a model of type (a), Section 3, with $\omega=-\omega'$, $|\omega|\leqq 35.3°$, and possibly $\omega=\omega'=0$.

With all three variants (i–ii–iii) of the H-M method, one electron of CH_3 is more loosely bound than the rest. In fact, in (ii) one root is nonbonding, and in (i) nearly so. The H-L-P-S method also predicts one loose electron in CH_3, *viz.*, that electron of C which is unpaired to an H partner. Experimental confirmation is provided by the fact that the ionization potential 10.3 volts of CH_3 is lower than that, 14.5, of CH_4, an observation due to Mulliken.[23] From qualitative consideration of the wave functions, he has, in fact, suggested a pyramidal model of CH_3 with one loosely held electron.

[23] R. S. Mulliken, Phys. Rev. **40**, 56 (1932).

The Quantum Mechanics of Seven and Eight Electrons with Spin Degeneracy

HENRY EYRING AND GEORGE E. KIMBALL, *Frick Chemical Laboratory, Princeton University*

(Received January 27, 1933)

The eigenfunctions corresponding to the fourteen singlet states of a system of seven or eight electrons are given and the corresponding matrix elements tabulated in a form convenient for computation, neglecting multiple interchange integrals. Proof is given that the general method described in earlier work for writing bond eigenfunctions suffices to separate the multiplets. A method for calculating matrix components between bond eigenfunctions directly from the bond systems is also described.

IN a series of papers from this laboratory[1] the problem of five or six spherically symmetric atoms, each with one valence electron, has been solved to the first order of the perturbation theory of quantum mechanics and the results applied to the calculation of the activation energies of some typical chemical reactions. In the third paper of this series it was found to be necessary to extend the results to the case of eight atoms. In this paper we shall give the details of these calculations and at the same time supply proofs of certain theorems which were assumed in the earlier papers of this series.

The method of approach is an extension of a method used by Slater[2] for the problems of three and four atoms. Since the seven-electron problem is immediately obtained from the eight-electron problem by putting one electron at infinity, it need not be considered separately. Let the eigenfunctions (neglecting spin) of the eight atoms be $a(x, y, z)$, $b(x, y, z)$, $\cdots$, $h(x, y, z)$. Let the coordinates of the eight electrons be $x_1, y_1, z_1, x_2, \cdots, z_8$. We shall abbreviate such an expression as $a(x_1, y_1, z_1)$ to $a(1)$. Then an approximate solution of the problem of eight atoms is the eigenfunction $a(1)b(2)c(3)\cdots h(8)$. Any function which may be obtained from this by permuting the numbers 1 to 8 is an equally good solution.

If we now introduce the spin of the electron, we find that instead of the 8! solutions we have just obtained, we have $2^8 8!$ solutions since with each space eigenfunction we may either associate the eigenfunction α representing the electron spin of $+1/2\ h/2\pi$ or the eigenfunction β representing a spin of $-1/2\ h/2\pi$. The Pauli exclusion principle, however, limits us to the 2^8 linear combinations of these eigenfunctions which are antisymmetric in the electrons. Following Slater, we shall take as these antisymmetric combinations the determinant

$$\frac{1}{(8!)^{\frac{1}{2}}}\begin{vmatrix} a\alpha(1) & b\alpha(1) & \cdots & h\alpha(1) \\ a\alpha(2) & b\alpha(2) & \cdots & h\alpha(2) \\ \cdot & \cdot & \cdot & \cdot \\ a\alpha(8) & b\alpha(8) & \cdots & h\alpha(8) \end{vmatrix} \tag{1}$$

and the 2^8-1 determinants which may be obtained from this by replacing any column or columns of α's by β's. We shall denote such an eigenfunction by a symbol such as

$$\begin{pmatrix} a & b & c & d & e & f & g & h \\ \alpha & \alpha & \beta & \alpha & \alpha & \beta & \alpha & \alpha \end{pmatrix},$$

this denoting that determinant in which the c and f columns contain β's and the rest α's.

Each of these eigenfunctions is an exact eigenfunction of S_z, the operator giving the total z-component of spin, since each term of the expansion of the determinant is an eigenfunction of S_z with the same eigenvalue. We may, therefore, classify these eigenfunctions according to their values of S_z, which are easily seen to be $(n_\alpha - n_\beta) \times h/4\pi$ where n_α is the number of columns of α's and n_β is the number of columns of β's. The number of eigenfunctions with each value of S_z is given in Table I. By a well-known theorem, if

[1] Sherman and Eyring, J. Am. Chem. Soc. **54**, 2661 (1932); Kimball and Eyring, J. Am. Chem. Soc. **54**, 3876 (1932); Taylor, Eyring and Sherman, J. Chem. Phys. **1**, 68 (1933).

[2] Slater, Phys. Rev. **38**, 1109 (1931).

spin interactions are neglected the matrix elements of the Hamiltonian operator H between eigenfunctions with different values of S_z all vanish, so that in the perturbation theory we can consider each group separately, instead of using all 256 eigenfunctions at once.

TABLE I.

S_z (in units $h/2\pi$)	4	3	2	1	0	−1	−2	−3	−4
No. eigenfunctions	1	8	28	56	70	56	28	8	1

Although these eigenfunctions are eigenfunctions of S_z, they are not in general eigenfunctions of S^2, the square of the total angular momentum. It is possible, however, to combine these eigenfunctions in such a way that the new eigenfunctions are eigenfunctions of S^2 as well. Consider, for example, the 70 eigenfunctions for which $S_z=0$. We shall show that from this set we can form 70 linear combinations which are, of course, still eigenfunctions of S_z and in addition are now eigenfunctions of S^2. Of these new eigenfunctions, 1 will have the eigenvalue $20(h/2\pi)^2$, 7 the eigenvalue $12(h/2\pi)^2$, 20 the eigenvalue $6(h/2\pi)^2$, 28 the eigenvalue $2(h/2\pi)^2$ and 14 the eigenvalue 0. Moreover, these eigenfunctions will have no matrix elements of H between the various groups.

In order to find these combinations we define for each pair of atoms ab, ac, etc., a function $\delta_{ab}(k)$. This function $\delta_{ab}(k)$ has the value 1 if in the k^{th} eigenfunction in the set of 70 the spin of a is α and the spin of b is β; it has the value -1 if the spin of a is β and the spin of b is α; and it has the value 0 if a and b have the same spin. By means of these functions we may construct an eigenfunction corresponding to any way of drawing bonds between the eight atoms. Suppose, for example, that we wish the eigenfunction corresponding to the bonds a–b c–d e–f g–h. The required eigenfunction is then

$$\sum_k \delta_{ab}(k)\delta_{cd}(k)\delta_{ef}(k)\delta_{gh}(k)\psi_k,$$

where ψ_k is the k^{th} eigenfunction in the original set of 70. Although there are 105 ways of drawing 4 bonds between 8 atoms, only 14 of the resulting eigenfunctions are linearly independent.

We shall now show that these bond eigenfunctions are eigenfunctions of S^2. By definition

$$S^2=S_x^2+S_y^2+S_z^2. \tag{2}$$

Remembering the commutation rules

$$\begin{aligned} S_xS_y-S_yS_x&=ih/2\pi \quad S_z\\ S_yS_z-S_zS_y&=ih/2\pi \quad S_x\\ S_zS_x-S_xS_z&=ih/2\pi \quad S_y \end{aligned}$$

we may write (2) in the form

$$S^2=(S_x+iS_y)(S_x-iS_y)-h/2\pi S_z+S_z^2 \tag{3a}$$

or

$$S^2=(S_x-iS_y)(S_x+iS_y)+h/2\pi S_z+S_z^2. \tag{3b}$$

It follows that if a function is an eigenfunction of S_z and S^2 it must also be an eigenfunction of $(S_x+iS_y)(S_x-iS_y)$ and of $(S_x-iS_y)(S_x+iS_y)$. Now the operator

$$S_x+iS_y=S_{x1}+iS_{y1}+S_{x2}+iS_{y2}+\cdots+S_{x8}+iS_{y8}$$

where S_{x1} and S_{y1} are the operators for the x and y components of the spin of electron 1. Since[3]

$$\begin{aligned} S_{x1}\alpha(1)&=(h/4\pi)\beta(1); \quad & S_{x1}\beta(1)&=(h/4\pi)\alpha(1)\\ S_{y1}\alpha(1)&=(ih/4\pi)\beta(1); \quad & S_{y1}\beta(1)&=(-ih/4\pi)\alpha(1) \end{aligned}$$

we have $(S_{x1}+iS_{y1})\alpha(1)=0$,

$(S_{x1}+iS_{y1})\beta(1)=(h/2\pi)\alpha(1)$,

and also $(S_{x1}-iS_{y1})\alpha(1)=(h/2\pi)\beta(1)$,

$(S_{x1}-iS_{y1})\beta(1)=0$.

Let us now consider the effect of the operator S_x+iS_y on a typical Slater eigenfunction. Acting on

$$\begin{pmatrix} a & b & c & d & e & f & g & h\\ \alpha & \alpha & \alpha & \alpha & \alpha & \alpha & \alpha & \alpha \end{pmatrix}$$

the operator S_x+iS_y obviously gives 0. Acting on any other eigenfunction of this type it is easily seen that the result is $h/2\pi$ times the sum of all the determinants which may be obtained by replacing one column of β's by α's. Thus

$$(S_x+iS_y)\begin{pmatrix} a & b & c & d & e & f & g & h\\ \beta & \beta & \alpha & \alpha & \alpha & \alpha & \alpha & \alpha \end{pmatrix}$$

$$=\frac{h}{2\pi}\begin{pmatrix} a & b & c & d & e & f & g & h\\ \alpha & \beta & \alpha & \alpha & \alpha & \alpha & \alpha & \alpha \end{pmatrix}+\frac{h}{2\pi}\begin{pmatrix} a & b & c & d & e & f & g & h\\ \beta & \alpha & \alpha & \alpha & \alpha & \alpha & \alpha & \alpha \end{pmatrix}.$$

[3] Pauli, Zeits. f. Physik 43, 601 (1927).

Similarly the operator $S_x - iS_y$ gives 0 when it acts on

$$\begin{pmatrix} a & b & c & d & e & f & g & h \\ \beta & \beta & \beta & \beta & \beta & \beta & \beta & \beta \end{pmatrix}$$

and acting on any other Slater eigenfunction gives $h/2\pi$ times the sum of all the determinants which may be obtained by replacing one column of α's by β's.

It is now easily verified that the operator $S_x + iS_y$ acting on any bond eigenfunction corresponding to four bonds gives 0 as a result. Hence, the operator $(S_x - iS_y)(S_x + iS_y)$ also gives 0, and since S_z operating on any of the set of 70 original eigenfunctions gives 0, it follows that the operator S^2 acting on this eigenfunction also gives 0. The bond eigenfunctions corresponding to 4 bonds are, therefore, eigenfunctions of S^2 with the eigenvalue 0. A similar argument shows that those bond eigenfunctions corresponding to 3 bonds are eigenfunctions of S^2 with the eigenvalue $2(h/2\pi)^2$, those corresponding to 2 bonds have the eigenvalue $6(h/2\pi)^2$, those corresponding to 1 bond have the eigenvalue $12(h/2\pi)^2$, and that the single eigenfunction corresponding to no bonds has the eigenvalue $20(h/2\pi)^2$. It follows that the matrix components of H between bond eigenfunctions corresponding to different numbers of bonds all vanish.

Since in chemical problems it is almost always the state of lowest multiplicity which is of interest, we may from now on confine our attention to a set of fourteen linearly independent bond eigenfunctions with $S_z = 0$ and $S^2 = 0$. The actual set of fourteen used were those corresponding to the ways of drawing the bonds shown in Table II.

TABLE II.

ψ_1	a–b c–d e–f g–h	ψ_8	a–c b–d e–g f–h
ψ_2	a–b c–e d–f g–h	ψ_9	a–c b–e d–g f–h
ψ_3	a–c b–d e–f g–h	ψ_{10}	a–d b–e c–g f–h
ψ_4	a–c b–e d–f g–h	ψ_{11}	a–h b–g c–d e–f
ψ_5	a–d b–e c–f g–h	ψ_{12}	a–h b–g c–e d–f
ψ_6	a–b c–d e–g f–h	ψ_{13}	a–h b–d c–g e–f
ψ_7	a–b c–e d–g f–h	ψ_{14}	a–b c–g d–h e–f

These eigenfunctions are independent, and since all other four-bond eigenfunctions can be expressed in terms of them they form a complete set.

By using these fourteen eigenfunctions as a basis for the usual perturbation theory, the energy is given to the first order by the secular equation

$$\begin{vmatrix} H_{1,1}-d_{1,1}E & H_{1,2}-d_{1,2}E & \cdots & H_{1,14}-d_{1,14}E \\ H_{2,1}-d_{2,1}E & H_{2,2}-d_{2,2}E & \cdots & H_{2,14}-d_{2,14}E \\ \cdot & \cdot & \cdot & \cdot \\ H_{14,1}-d_{14,1}E & H_{14,2}-d_{14,2}E & \cdots & H_{14,14}-d_{14,14}E \end{vmatrix} = 0, \tag{4}$$

where

$$H_{ij} = \int \psi_i^* H \psi_j d\tau, \quad d_{ij} = \int \psi_i^* \psi_j d\tau.$$

We must, therefore, evaluate these integrals.

We shall suppose that the field due to all the electrons in each atom except the valence electron may be represented by a function $V(x, y, z)$, distinguishing the atoms by subscripts as $V_a(x, y, z)$. Then the Hamiltonian function takes the form

$$H = \sum_{i=1}^{8} -h^2/8\pi^2 m \nabla_i^2 + \sum_{\nu=a,\, b,\, c \cdots} \sum_{i=1}^{8} V_\nu(x_i, y_i, z_i) + \sum_{j>i} (e^2/r_{ij}).$$

Since the eigenfunction $a(i)$ is by hypothesis a solution of the equation

$$(-h^2/8\pi^2 m \nabla_i^2 + V_a(x_i, y_i, z_i))a(i) = E_a a(i),$$

where E_a is the lowest energy level of atom a, we may replace the operator $-(h^2/8\pi^2 m)\nabla_i^2$ by $E_a - V_a(i)$ whenever it operates on $a(i)$ and by similar expressions when it operates on the other atomic eigenfunctions. The matrix components of H between the Slater eigenfunctions have been discussed by Slater.[2] If we neglect the lack of orthogonality of the eigenfunctions $a(i)$, $b(i)$, $c(i) \cdots$, the multiple interchange integrals are all small and can be neglected. To this degree of ap-

proximation the matrix components are then given by the following rules:

(1) The matrix component between any Slater eigenfunction and itself is the coulombic integral

$$C=\int a(1)b(2)\cdots h(8)IIa(1)b(2)\cdots h(8)d\tau$$

minus the sum of all the interchange integrals between atoms having the same spin. The interchange integral between two atoms, say a and b, is the integral

$$(ab)=\int a(1)b(2)\cdots h(8)IIb(1)a(2)\cdots h(8)d\tau.$$

(2) The matrix element between two different Slater eigenfunctions is zero unless the two eigenfunctions differ only by a single interchange of spins on two atoms, in which case the matrix component is the negative of the interchange integral between these two atoms. For example, the diagonal matrix element for the eigenfunction

$$\begin{pmatrix} a & b & c & d & e & f & g & h \\ \alpha & \alpha & \alpha & \alpha & \beta & \beta & \beta & \beta \end{pmatrix}$$

is $C-(ab)-(ac)-(ad)-(bc)-(bd)-(cd)-(ef)-(eg)-(eh)-(fg)-(fh)-(gh)$, while the matrix element between this and

$$\begin{pmatrix} a & b & c & d & e & f & g & h \\ \beta & \alpha & \alpha & \alpha & \alpha & \beta & \beta & \beta \end{pmatrix}$$

is $-(ae)$.

These rules enable us to find the matrix elements between the various bond eigenfunctions. Suppose, for example, that we wished to find the matrix element between the eigenfunction representing the bond system a–b c–d e–f g–h and that representing the bonds a–c b–d e–g f–h. We could, of course, actually write out these eigenfunctions in terms of the Slater eigenfunctions and, knowing the matrix components of H between these, find the required matrix element. It is, however, possible to set up rules for finding the matrix element directly. It is evident that the matrix element we seek will be the sum of some multiple of C and certain multiples of the various interchange integrals. We shall now show how the coefficients of the various integrals in the matrix element may be simply determined. Let us first consider C. The only way C can occur in the result is from the presence of the same Slater eigenfunction as a part of both bond eigenfunctions. The coefficient of C is, therefore, equal to the number of Slater eigenfunctions which occur once in each of the two bond eigenfunctions, taken with $a+$ or $-$ sign according to whether they occur with the same or opposite signs in the two bond eigenfunctions. In order to find this number we write the two bond systems above one another, thus:

$$\begin{array}{cccc} a\text{–}b & c\text{–}d & e\text{–}f & g\text{–}h \\ a\text{–}c & b\text{–}d & e\text{–}g & f\text{–}h. \end{array}$$

We now start assigning spins to the various atoms. Taking a arbitrarily to have the spin α, we must have the spin β on b in order to have the bond a–b. We, therefore, write α on the a's and β on the b's. In the same way we see that the spin of c must be β and that of d must be α. We now have the following picture:

$$\begin{array}{cccc} \alpha & \beta & \beta & \alpha \\ a\text{–}b & c\text{–}d & e\text{–}f & g\text{–}h \\ a\text{–}c & b\text{–}d & e\text{–}g & f\text{–}h \\ \alpha & \beta & \beta & \alpha. \end{array}$$

We may now choose the spin of e arbitrarily, but then all the spins are determined, thus:

$$\begin{array}{cccccccc} \alpha & \beta & \beta & \alpha & \alpha & \beta & \beta & \alpha \\ a\text{–}b & c\text{–}d & e\text{–}f & g\text{–}h & & & & \\ a\text{–}c & b\text{–}d & e\text{–}g & f\text{–}h & & & & \\ \alpha & \beta & \beta & \alpha & \alpha & \beta & \beta & \alpha. \end{array}$$

Since we could have chosen a to be either α or β, and likewise e to be either α or β, there are four Slater eigenfunctions common to the two bond eigenfunctions. It is easily seen that these eigenfunctions all enter both bond eigenfunctions with the same sign, so that the coefficient of C in the matrix element is $+4$.

In order to find the coefficient of an interchange integral such as (ab) we proceed in a similar way. We note first that such an integral can arise in two ways: it may arise from the presence of a Slater eigenfunction common to both eigenfunctions in which a and b have the same spin; or it may arise from the presence of two Slater eigenfunctions differing only in the interchange of the spins of a and b. The two cases are considered

separately. To obtain the contribution of the first case we again put down our two bond systems and now write α's on the a's and also on the b's. We then proceed to fix the other spins by the requirement that wherever there is a bond between two atoms the spins must be opposite. The process is continued until every spin is fixed or an inconsistency is reached. For example, taking the same bond system as before the result for (ab) is immediately inconsistent because of the bond a–b in the first eigenfunction. If we take the integral (ae), however, we find

$$\begin{array}{cccc} \alpha\ \beta & \beta\ \alpha & \alpha\ \beta & \beta\ \alpha \\ a\text{–}b & c\text{–}d & e\text{–}f & g\text{–}h \\ a\text{–}c & b\text{–}d & e\text{–}g & f\text{–}h \\ \alpha\ \beta & \beta\ \alpha & \alpha\ \beta & \beta\ \alpha. \end{array}$$

There are, therefore, only two Slater eigenfunctions giving rise to the integral (ae) (one with α's, the other with β's on a and e). Each has a positive sign, so that the contribution to the coefficient of (ae) is -2 (the negative sign arising from the original rules for matrix elements between Slater eigenfunctions). Taking the integral (ad) as a further example we find

$$\begin{array}{cccc} \alpha\ \beta & \beta\ \alpha & \alpha\ \beta & \beta\ \alpha \\ a\text{–}b & c\text{–}d & e\text{–}f & g\text{–}h \\ a\text{–}c & b\text{–}d & e\text{–}g & f\text{–}h \\ \alpha\ \beta & \beta\ \alpha & \alpha\ \beta & \beta\ \alpha. \end{array}$$

In this case, when the spins of a, b, c and d were assigned we were left free to choose either spin for e, so that there are four eigenfunctions giving the integral (ad). The contribution to the coefficient of (ad) is, therefore, -4.

In order to find the other part of the coefficient of (ab) we write α on a and β on b in the first bond system and β on a and α on β in the second, continuing the process as before. Thus we find

$$\begin{array}{cccc} \alpha\ \beta & \alpha\ \beta & \alpha\ \beta & \beta\ \alpha \\ a\text{–}b & c\text{–}d & e\text{–}f & g\text{–}h \\ a\text{–}c & b\text{–}d & e\text{–}g & f\text{–}h \\ \beta\ \alpha & \alpha\ \beta & \alpha\ \beta & \beta\ \alpha. \end{array}$$

The sign of the first is negative and the second positive, and we could have chosen α or β on a and also on e. The contribution is, therefore, $+4$. The total coefficient of (ab) is, therefore, $+4$. The diagrams for (ae) and (ad) and their contributions are

$$(ae)\qquad \begin{array}{cccc} \alpha\ \beta & \beta\ \alpha & \beta & \\ a\text{–}b & c\text{–}d & e\text{–}f & g\text{–}h \\ a\text{–}c & b\text{–}d & e\text{–}g & f\text{–}h \\ \beta\ \beta & \alpha\ \alpha & & \end{array} \qquad \text{(inconsistent)}$$

$$(ad)\qquad \begin{array}{cccc} \alpha\ \beta & \alpha\ \beta & \alpha\ \beta & \beta\ \alpha \\ a\text{–}b & c\text{–}d & e\text{–}f & g\text{–}h \\ a\text{–}c & b\text{–}d & e\text{–}g & f\text{–}h \\ \beta\ \alpha & \beta\ \alpha & \alpha\ \beta & \beta\ \alpha. \end{array} \qquad (-4)$$

The total coefficient of (ae) is, therefore, -2 and that of (ad), -8.

TABLE III.

$$\begin{aligned}
\chi_1 &= \psi_1 \\
\chi_2 &= \psi_2 - \tfrac{1}{2}\psi_1 \\
\chi_3 &= \psi_3 - \tfrac{1}{2}\psi_1 \\
\chi_4 &= \psi_4 - \tfrac{1}{2}\psi_3 - \tfrac{1}{2}\psi_2 + \tfrac{1}{4}\psi_1 \\
\chi_5 &= \psi_5 - \tfrac{1}{3}\psi_4 - \tfrac{1}{3}\psi_3 - \tfrac{1}{3}\psi_2 + \tfrac{2}{3}\psi_1 \\
\chi_6 &= \psi_6 - \tfrac{1}{2}\psi_1 \\
\chi_7 &= \psi_7 - \tfrac{1}{2}\psi_6 - \tfrac{1}{2}\psi_2 + \tfrac{1}{4}\psi_1 \\
\chi_8 &= \psi_8 - \tfrac{1}{2}\psi_6 - \tfrac{1}{2}\psi_3 + \tfrac{1}{4}\psi_1 \\
\chi_9 &= \psi_9 - \tfrac{1}{2}\psi_8 - \tfrac{1}{2}\psi_7 + \tfrac{1}{4}\psi_6 - \tfrac{1}{2}\psi_4 + \tfrac{1}{4}\psi_3 + \tfrac{1}{4}\psi_2 - \tfrac{1}{8}\psi_1 \\
\chi_{10} &= \psi_{10} - \tfrac{1}{3}\psi_9 - \tfrac{1}{3}\psi_8 - \tfrac{1}{3}\psi_7 + \tfrac{2}{3}\psi_6 - \tfrac{1}{2}\psi_5 + \tfrac{1}{6}\psi_4 + \tfrac{1}{6}\psi_3 + \tfrac{1}{6}\psi_2 - \tfrac{1}{3}\psi_1 \\
\chi_{11} &= \psi_{11} - \tfrac{2}{3}\psi_{10} + \tfrac{2}{3}\psi_9 - \tfrac{1}{3}\psi_6 + \tfrac{1}{3}\psi_5 - \tfrac{1}{3}\psi_4 - \tfrac{1}{3}\psi_1 \\
\chi_{12} &= \psi_{12} - \tfrac{1}{2}\psi_{11} - \tfrac{1}{3}\psi_{10} - \tfrac{1}{3}\psi_9 + \tfrac{2}{3}\psi_8 + \tfrac{1}{3}\psi_7 - \tfrac{1}{2}\psi_6 + \tfrac{1}{6}\psi_5 + \tfrac{1}{6}\psi_4 - \tfrac{1}{3}\psi_3 - \tfrac{2}{3}\psi_2 + \tfrac{1}{3}\psi_1 \\
\chi_{13} &= \psi_{13} + \tfrac{1}{3}\psi_{12} - \tfrac{2}{3}\psi_{11} - \tfrac{4}{5}\psi_{10} - \tfrac{4}{5}\psi_9 + \tfrac{2}{5}\psi_8 + \tfrac{7}{5}\psi_7 - \tfrac{2}{3}\psi_6 + \tfrac{2}{5}\psi_5 + \tfrac{2}{5}\psi_4 - \tfrac{7}{5}\psi_3 - \tfrac{2}{5}\psi_2 + \tfrac{2}{3}\psi_1 \\
\chi_{14} &= \psi_{14} - \tfrac{3}{4}\psi_{13} - \tfrac{1}{4}\psi_{12} + \tfrac{1}{2}\psi_{11} + \tfrac{1}{3}\psi_{10} + \tfrac{1}{3}\psi_9 - \tfrac{5}{12}\psi_8 + \tfrac{1}{12}\psi_7 + \tfrac{1}{6}\psi_6 - \tfrac{1}{6}\psi_5 - \tfrac{1}{6}\psi_4 + \tfrac{7}{12}\psi_3 + \tfrac{1}{12}\psi_2 - \tfrac{5}{8}\psi_1
\end{aligned}$$

TABLE IV.

	$H_{1,1}$	$H_{1,2}$	$H_{1,3}$	$H_{1,4}$	$H_{1,5}$	$H_{1,6}$	$H_{1,7}$	$H_{1,8}$	$H_{1,9}$	$H_{1,10}$	$H_{1,11}$	$H_{1,12}$	$H_{1,13}$	$H_{1,14}$	$H_{2,2}$	$H_{2,3}$	$H_{2,4}$	$H_{2,5}$	$H_{2,6}$	$H_{2,7}$	$H_{2,8}$	$H_{2,9}$	$H_{2,10}$	$H_{2,11}$	$H_{2,12}$	$H_{2,13}$	$H_{2,14}$	$H_{3,3}$
C	8	0	0	0	0	0	0	0	0	0	0	0	0	0	6	0	0	0	0	0	0	0	0	0	0	0	0	6
ab	8	0	0	0	0	0	0	0	0	0	0	0	0	0	6	0	0	0	0	0	0	0	0	0	0	0	0	−6
ac	−4	0	6	0	0	0	0	0	0	0	0	0	0	0	−3	0	9/2	0	0	0	0	0	0	0	0	0	0	3
ad	−4	0	−6	0	0	0	0	0	0	0	0	0	0	0	−3	0	3/2	0	0	0	0	0	0	0	0	0	0	3
ae	−4	0	0	−3	4	0	0	0	0	0	0	0	0	0	−3	−3	−3	2	0	0	0	0	0	0	0	0	0	−3
af	−4	0	0	3	−4	0	0	0	0	0	0	0	0	0	−3	3	−3	−2	0	0	0	0	0	0	0	0	0	−3
ag	−4	0	0	0	0	0	0	0	3/2	−2	−4	0	0	0	−3	0	0	0	0	0	3/2	−3/2	−1	0	−3	0	0	−3
ah	−4	0	0	0	0	0	0	0	−3/2	2	4	0	0	0	−3	0	0	0	0	0	−3/2	3/2	1	0	3	0	0	−3
bc	−4	0	−6	0	0	0	0	0	0	0	0	0	0	0	−3	0	−9/2	0	0	0	0	0	0	0	0	0	0	3
bd	−4	0	6	0	0	0	0	0	0	0	0	0	0	0	−3	0	−3/2	0	0	0	0	0	0	0	0	0	0	3
be	−4	0	0	3	−4	0	0	0	0	0	0	0	0	0	−3	3	3	2	0	0	0	0	0	0	0	0	0	−3
bf	−4	0	0	−3	4	0	0	0	0	0	0	0	0	0	−3	−3	3	−2	0	0	0	0	0	0	0	0	0	−3
bg	−4	0	0	0	0	0	0	0	−3/2	2	4	0	0	0	−3	0	0	0	0	0	−3/2	3/2	1	0	3	0	0	−3
bh	−4	0	0	0	0	0	0	0	3/2	−2	−4	0	0	0	−3	0	0	0	0	0	3/2	−3/2	−1	0	−3	0	0	−3
cd	8	0	0	0	0	0	0	0	0	0	0	0	0	0	−6	0	0	0	0	0	6	0	0	0	0	0	0	−6
ce	−4	6	0	0	0	0	0	0	0	0	0	0	0	0	3	0	0	−4	0	0	0	0	0	0	0	0	0	−3
cf	−4	−6	0	0	0	0	0	0	0	0	0	0	0	0	3	0	0	4	0	0	0	0	0	0	0	0	0	−3
cg	−4	0	0	0	0	0	−3	0	0	0	0	0	2	5/2	−3	0	0	0	−3	3	0	0	0	0	0	1	5/4	−3
ch	−4	0	0	0	0	0	3	0	0	0	0	0	−2	−5/2	−3	0	0	0	3	−3	0	0	0	0	0	−1	−5/4	−3
de	−4	−6	0	0	0	0	0	0	0	0	0	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	0	−3
df	−4	6	0	0	0	0	0	0	0	0	0	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	0	−3
dg	−4	0	0	0	0	0	3	0	0	0	0	0	−2	−5/2	−3	0	0	0	3	3	0	0	0	0	0	1	5/4	−3
dh	−4	0	0	0	0	0	−3	0	0	0	0	0	2	5/2	−3	0	0	0	−3	−3	0	0	0	0	0	−1	−5/4	−3
ef	8	0	0	0	0	0	0	0	0	0	0	0	0	0	−6	0	0	0	0	0	0	0	0	0	0	0	0	6
eg	−4	0	0	0	0	6	0	0	0	0	0	0	0	0	−3	0	0	0	0	−3/2	0	0	0	0	0	−2	−5/2	−3
eh	−4	0	0	0	0	−6	0	0	0	0	0	0	0	0	−3	0	0	0	0	3/2	0	0	0	0	0	2	5/2	−3
fg	−4	0	0	0	0	−6	0	0	0	0	0	0	0	0	−3	0	0	0	0	−9/2	0	0	0	0	0	0	0	−3
fh	−4	0	0	0	0	6	0	0	0	0	0	0	0	0	−3	0	0	0	0	9/2	0	0	0	0	0	0	0	−3
gh	8	0	0	0	0	0	0	0	0	0	0	0	0	0	6	0	0	0	0	0	0	0	0	0	0	0	0	6

	$H_{3,4}$	$H_{3,5}$	$H_{3,6}$	$H_{3,7}$	$H_{3,8}$	$H_{3,9}$	$H_{3,10}$	$H_{3,11}$	$H_{3,12}$	$H_{3,13}$	$H_{3,14}$	$H_{4,4}$	$H_{4,5}$	$H_{4,6}$	$H_{4,7}$	$H_{4,8}$	$H_{4,9}$	$H_{4,10}$	$H_{4,11}$	$H_{4,12}$	$H_{4,13}$	$H_{4,14}$	$H_{5,5}$	$H_{5,6}$	$H_{5,7}$	$H_{5,8}$	$H_{5,9}$	$H_{5,10}$
C	0	0	0	0	0	0	0	0	0	0	0	9/2	0	0	0	0	0	0	0	0	0	0	4	0	0	0	0	0
ab	0	0	0	0	0	0	0	0	0	0	0	−9/2	0	0	0	0	0	0	0	0	0	0	−4	0	0	0	0	0
ac	0	0	0	0	0	0	0	0	0	0	0	9/4	0	0	0	0	0	0	0	0	0	0	−4	0	0	0	0	0
ad	0	0	0	0	0	0	0	0	0	0	0	−15/4	2	0	0	0	0	0	0	0	0	0	4/3	0	0	0	0	0
ae	3	2	0	0	0	0	0	0	0	0	0	3/4	−1	0	0	0	0	0	0	0	0	0	4/3	0	0	0	0	0
af	−3	−2	0	0	0	0	0	0	0	0	0	3/4	−1	0	0	0	0	0	0	0	0	0	4/3	0	0	0	0	0
ag	0	0	0	3/2	0	−3/2	−1	0	1	−8/3	0	−9/4	0	3/2	−3/2	−3/2	3/2	−1/2	1	−1	−4/3	0	−2	−2	−1	−1	−1/2	5/3
ah	0	0	0	−3/2	0	3/2	1	0	−1	8/3	0	−9/4	0	−3/2	3/2	3/2	−3/2	1/2	−1	1	4/3	0	−2	2	1	1	1/2	−5/3
bc	0	0	0	0	0	0	0	0	0	0	0	9/4	0	0	0	0	0	0	0	0	0	0	−4	0	0	0	0	0
bd	0	0	0	0	0	0	0	0	0	0	0	−15/4	2	0	0	0	0	0	0	0	0	0	4/3	0	0	0	0	0
be	3	2	0	0	0	0	0	0	0	0	0	3/4	−1	0	0	0	0	0	0	0	0	0	4/3	0	0	0	0	0
bf	−3	−2	0	0	0	0	0	0	0	0	0	3/4	−1	0	0	0	0	0	0	0	0	0	4/3	0	0	0	0	0
bg	0	0	0	−3/2	0	−3/2	−1	0	1	−2/3	5/2	−9/4	0	−3/2	3/2	−3/2	3/2	−1/2	1	−1	−1/3	5/4	−2	2	1	−1	−1/2	5/3
bh	0	0	0	3/2	0	3/2	1	0	−1	2/3	−5/2	−9/4	0	3/2	−3/2	3/2	−3/2	1/2	−1	1	1/3	−5/4	−2	−2	−1	1	1/2	−5/3
cd	0	0	0	0	0	0	0	0	0	0	0	−3/2	−4	0	0	0	0	0	0	0	0	0	4/3	0	0	0	0	0
ce	−3/2	−4	0	0	0	0	0	0	0	0	0	−15/4	2	0	0	0	0	0	0	0	0	0	4/3	0	0	0	0	0
cf	3/2	4	0	0	0	0	0	0	0	0	0	−15/4	2	0	0	0	0	0	0	0	0	0	4/3	0	0	0	0	0
cg	0	0	0	0	0	3/4	2	2	−1	5/3	−5/4	−9/4	0	0	0	3/4	−3/4	1	−1	5/2	5/6	−5/8	−2	0	0	2	1	5/3
ch	0	0	0	0	0	−3/4	−2	−2	1	−5/3	5/4	−9/4	0	0	0	−3/4	3/4	−1	1	−5/2	−5/6	5/8	−2	0	0	−2	−1	−5/3
de	−9/2	0	0	0	0	0	0	0	0	0	0	9/4	0	0	0	0	0	0	0	0	0	0	−4	0	0	0	0	0
df	9/2	0	0	0	0	0	0	0	0	0	0	9/4	0	0	0	0	0	0	0	0	0	0	−4	0	0	0	0	0
dg	0	0	0	0	0	9/4	0	−2	−1	5/3	−5/4	−9/4	0	0	0	9/4	9/4	0	1	1/2	−5/6	5/8	−2	0	0	0	0	−1
dh	0	0	0	0	0	−9/4	0	2	1	−5/3	5/4	−9/4	0	0	0	−9/4	−9/4	0	−1	−1/2	5/6	−5/8	−2	0	0	0	0	1
ef	0	0	0	0	0	0	0	0	0	0	0	−9/2	0	0	0	0	0	0	0	0	0	0	−4	0	0	0	0	0
eg	0	0	0	0	9/2	0	0	0	0	0	0	−9/4	0	0	0	0	−9/8	0	−2	−1	5/3	−5/4	−2	0	0	0	0	−1
eh	0	0	0	0	−9/2	0	0	0	0	0	0	−9/4	0	0	0	0	9/8	0	2	1	−5/3	5/4	−2	0	0	0	0	1
fg	0	0	0	0	−9/2	0	0	0	0	0	0	−9/4	0	0	0	0	−27/8	0	0	0	0	0	−2	0	0	0	0	−3
fh	0	0	0	0	9/2	0	0	0	0	0	0	−9/4	0	0	0	0	27/8	0	0	0	0	0	−2	0	0	0	0	3
gh	0	0	0	0	0	0	0	0	0	0	0	9/2	0	0	0	0	0	0	0	0	0	0	4	0	0	0	0	0

TABLE IV. (*Continued*).

	$H_{5,11}$	$H_{5,12}$	$H_{5,13}$	$H_{5,14}$	$H_{6,6}$	$H_{6,7}$	$H_{6,8}$	$H_{6,9}$	$H_{6,10}$	$H_{6,11}$	$H_{6,12}$	$H_{6,13}$	$H_{6,14}$	$H_{7,7}$	$H_{7,8}$	$H_{7,9}$	$H_{7,10}$	$H_{7,11}$	$H_{7,12}$	$H_{7,13}$	$H_{7,14}$	$H_{8,8}$	$H_{8,9}$	$H_{8,10}$	$H_{8,11}$
C	0	0	0	0	6	0	0	0	0	0	0	0	0	9/2	0	0	0	0	0	0	0	9/2	0	0	0
ab	0	0	0	0	6	0	0	0	0	0	0	0	0	9/2	0	0	0	0	0	0	0	−9/2	0	0	0
ac	0	0	0	0	−3	0	9/2	0	0	0	0	0	0	−9/4	0	27/8	0	0	0	0	0	9/4	0	0	0
ad	0	0	0	0	−3	0	−9/2	0	0	0	0	0	0	−9/4	0	9/8	3	0	0	0	0	9/4	0	0	0
ae	0	0	0	0	−3	0	0	−9/4	3	0	0	0	0	−9/4	−9/4	−9/4	−3/2	0	0	0	0	−9/4	9/4	3/2	0
af	0	0	0	0	−3	0	0	−3/4	1	−4	0	0	0	−9/4	−3/4	3/4	1/2	0	−3	0	0	−9/4	3/4	1/2	0
ag	−4/3	−2/3	−8/9	0	−3	0	0	3/2	−2	2	0	0	0	−9/4	3/2	−3/2	−1	0	3/2	0	0	−9/4	−3/2	−1	0
ah	4/3	2/3	8/9	0	−3	0	0	3/2	−2	2	0	0	0	−9/4	3/2	−3/2	−1	0	3/2	0	0	−9/4	−3/2	−1	0
bc	0	0	0	0	−3	0	−9/2	0	0	0	0	0	0	−9/4	0	−27/8	0	0	0	0	0	9/4	0	0	0
bd	0	0	0	0	−3	0	9/2	0	0	0	0	0	0	−9/4	0	−9/8	−3	0	0	0	0	9/4	0	0	0
be	0	0	0	0	−3	0	0	9/4	−3	0	0	0	0	−9/4	9/4	9/4	3/2	0	0	0	0	−9/4	9/4	3/2	0
bf	0	0	0	0	−3	0	0	3/4	−1	4	0	0	0	−9/4	3/4	−3/4	−1/2	0	3	0	0	−9/4	3/4	1/2	0
bg	−4/3	−2/3	−2/9	5/6	−3	0	0	−3/2	2	−2	0	0	0	−9/4	−3/2	3/2	1	0	−3/2	0	0	−9/4	−3/2	−1	0
bh	4/3	2/3	2/9	−5/6	−3	0	0	−3/2	2	−2	0	0	0	−9/4	−3/2	3/2	1	0	−3/2	0	0	−9/4	−3/2	−1	0
cd	0	0	0	0	6	0	0	0	0	0	0	0	0	−9/2	0	0	0	0	0	0	0	−9/2	0	0	0
ce	0	0	0	0	−3	9/2	0	0	0	0	0	0	0	9/4	0	0	0	0	0	0	0	−9/4	−9/8	−3	0
cf	0	0	0	0	−3	3/2	0	0	0	0	0	2	5/2	−15/4	0	0	0	0	0	1	5/4	−9/4	−3/8	−1	2
cg	−2/3	−1/3	−10/9	5/6	−3	−3	0	0	0	0	0	−1	−5/4	3/4	0	0	0	0	0	−1/2	−5/8	−9/4	3/4	2	−1
ch	2/3	1/3	10/9	−5/6	−3	−3	0	0	0	0	0	−1	−5/4	3/4	0	0	0	0	0	−1/2	−5/8	−9/4	3/4	2	−1
de	0	0	0	0	−3	−9/2	0	0	0	0	0	0	0	9/4	0	0	0	0	0	0	0	−9/4	−27/8	0	0
df	0	0	0	0	−3	−3/2	0	0	0	0	0	−2	−5/2	−15/4	0	0	0	0	0	1	5/4	−9/4	−9/8	0	−2
dg	2/3	7/3	10/9	−5/6	−3	3	0	0	0	0	0	1	5/4	3/4	0	0	0	0	0	−1/2	−5/8	−9/4	9/4	0	1
dh	−2/3	−7/3	−10/9	5/6	−3	3	0	0	0	0	0	1	5/4	3/4	0	0	0	0	0	−1/2	−5/8	−9/4	9/4	0	1
ef	0	0	0	0	−6	0	0	0	0	0	0	0	0	−3/2	0	0	0	0	0	−2	−5/2	−9/2	0	0	0
eg	8/3	−2/3	10/9	−5/6	3	0	0	0	0	0	0	0	0	−15/4	0	0	0	0	0	1	5/4	9/4	0	0	0
eh	−8/3	2/3	−10/9	5/6	3	0	0	0	0	0	0	0	0	−15/4	0	0	0	0	0	1	5/4	9/4	0	0	0
fg	0	0	0	0	3	0	0	0	0	0	0	0	0	9/4	0	0	0	0	0	0	0	9/4	0	0	0
fh	0	0	0	0	3	0	0	0	0	0	0	0	0	9/4	0	0	0	0	0	0	0	9/4	0	0	0
gh	0	0	0	0	−6	0	0	0	0	0	0	0	0	−9/2	0	0	0	0	0	0	0	−9/2	0	0	0

	$H_{5,12}$	$H_{5,13}$	$H_{5,14}$	$H_{9,9}$	$H_{9,10}$	$H_{9,11}$	$H_{9,12}$	$H_{9,13}$	$H_{9,14}$	$H_{10,10}$	$H_{10,11}$	$H_{10,12}$	$H_{10,13}$	$H_{10,14}$	$H_{11,11}$	$H_{11,12}$	$H_{11,13}$	$H_{11,14}$	$H_{12,12}$	$H_{12,13}$	$H_{12,14}$	$H_{13,13}$	$H_{13,14}$	$H_{14,14}$
C	0	0	0	27/8	0	0	0	0	0	3	0	0	0	0	4	0	0	0	3	0	0	8/3	0	5/4
ab	0	0	0	−27/8	0	0	0	0	0	−3	0	0	0	0	−4	0	0	0	−3	0	0	−2/3	5/2	5/8
ac	0	0	0	27/16	0	0	0	0	0	−3	0	0	0	0	−2	1	−2/3	5/2	−5/2	−1/3	5/4	−22/9	−5/6	5/8
ad	0	0	0	−45/16	3/2	0	0	0	0	1	0	0	0	0	−2	−1	2/3	−5/2	−5/2	−1/3	5/4	−22/9	−5/6	5/8
ae	0	0	0	9/16	−3/4	0	0	0	0	1	0	0	0	0	−4	0	0	0	−1	2/3	−5/2	−22/9	−5/6	5/8
af	1	−8/3	0	−39/16	1/4	1	−1	−4/3	0	−7/3	−4/3	−2/3	−8/9	0	4/3	0	0	0	1	0	0	8/9	0	−5/2
ag	−1/2	4/3	0	−3/16	−1/2	−1/2	1/2	2/3	0	1/6	2/3	1/3	4/9	0	4/3	0	0	0	1	0	0	8/9	0	−5/2
ah	−1/2	4/3	0	−3/16	−1/2	−1/2	1/2	2/3	0	1/6	2/3	1/3	4/9	0	4/3	0	0	0	1	0	0	8/9	0	−5/2
bc	0	0	0	27/16	0	0	0	0	0	−3	0	0	0	0	−2	1	−8/3	0	−5/2	−4/3	0	8/9	0	−5/2
bd	0	0	0	−45/16	3/2	0	0	0	0	1	0	0	0	0	−2	−1	8/3	0	−5/2	−4/3	0	8/9	0	−5/2
be	0	0	0	9/16	−3/4	0	0	0	0	1	0	0	0	0	−4	0	0	0	−1	8/3	0	8/9	0	−5/2
bf	1	−2/3	5/2	−39/16	1/4	1	−1	−1/3	5/4	−7/3	−4/3	−2/3	−2/9	5/6	4/3	0	0	0	1	0	0	−22/9	−5/6	5/8
bg	−1/2	1/3	−5/4	−3/16	−1/2	−1/2	1/2	1/6	−5/8	1/6	2/3	1/3	1/9	−5/12	4/3	0	0	0	1	0	0	−22/9	−5/6	5/8
bh	−1/2	1/3	−5/4	−3/16	−1/2	−1/2	1/2	1/6	−5/8	1/6	2/3	1/3	1/9	−5/12	4/3	0	0	0	1	0	0	−22/9	−5/6	5/8
cd	0	0	0	−9/8	−3	0	0	0	0	1	0	0	0	0	4	0	0	0	−3	0	0	−8/3	0	−5/2
ce	0	0	0	−45/16	3/2	0	0	0	0	1	0	0	0	0	−2	3	0	0	3/2	0	0	−8/3	0	−5/2
cf	−1	5/3	−5/4	−21/16	−1/2	−1	5/2	5/6	−5/8	−7/3	−2/3	−1/3	−10/9	5/6	−2	−5/3	10/9	−5/6	1/6	5/9	−5/12	14/27	5/18	5/8
cg	1/2	−5/6	5/8	−39/16	1	1/2	−5/4	−5/12	5/16	1/6	1/3	1/6	5/9	−5/12	−2	−5/3	10/9	−5/6	1/6	5/9	−5/12	14/27	5/18	5/8
ch	1/2	−5/6	5/8	−39/16	1	1/2	−5/4	−5/12	5/16	1/6	1/3	1/6	5/9	−5/12	−2	−5/3	10/9	−5/6	1/6	5/9	−5/12	14/27	5/18	5/8
de	0	0	0	27/16	0	0	0	0	0	−3	0	0	0	0	−2	−3	0	0	3/2	0	0	−8/3	0	−5/2
df	−1	5/3	−5/4	−45/16	0	1	1/2	−5/6	5/8	−1	2/3	7/3	10/9	−5/6	−2	5/3	−10/9	5/6	1/6	5/9	−5/12	14/27	5/18	5/8
dg	1/2	−5/6	5/8	9/16	0	−1/2	−1/4	5/12	−5/16	−5/2	−1/3	−7/6	−5/9	5/12	−2	5/3	−10/9	5/6	1/6	5/9	−5/12	14/27	5/18	5/8
dh	1/2	−5/6	5/8	9/16	0	−1/2	−1/4	5/12	−5/16	−5/2	−1/3	−7/6	−5/9	5/12	−2	5/3	−10/9	5/6	1/6	5/9	−5/12	14/27	5/18	5/8
ef	0	0	0	−9/8	0	−2	−1	5/3	−5/4	−1	8/3	−2/3	10/9	−5/6	4/3	0	0	0	−7/3	−10/9	5/6	14/27	5/18	5/8
eg	0	0	0	−45/16	0	1	1/2	−5/6	5/8	−5/2	−4/3	1/3	−5/9	5/12	4/3	0	0	0	−7/3	−10/9	5/6	14/27	5/18	5/8
eh	0	0	0	−45/16	0	1	1/2	−5/6	5/8	−5/2	−4/3	1/3	−5/9	5/12	4/3	0	0	0	−7/3	−10/9	5/6	14/27	5/18	5/8
fg	0	0	0	27/16	0	0	0	0	0	3/2	0	0	0	0	−4	0	0	0	−3	0	0	−8/3	0	−5/2
fh	0	0	0	27/16	0	0	0	0	0	3/2	0	0	0	0	−4	0	0	0	−3	0	0	−8/3	0	−5/2
gh	0	0	0	−27/8	0	0	0	0	0	−3	0	0	0	0	−4	0	0	0	−3	0	0	−8/3	0	−5/2

Having found the matrix of H in this way it is a simple matter to find the matrix of unity, for if we neglect the integrals arising from the lack of orthogonality of the eigenfunctions, d_{ij} is just the coefficient of C in H_{ij}. If the various interchange integrals and the coulombic integral can be found, we can, therefore, set up the secular equation and complete the first order perturbation theory.

Since the bond eigenfunctions are not orthogonal, the secular equation contains E in every element. It is more convenient for numerical work to orthogonalize the fourteen bond eigenfunctions. The set of orthogonalized eigenfunctions is shown in Table III. The first eigenfunction in this table is just the first of the set of bond eigenfunctions of Table II. Each succeeding one is obtained by orthogonalizing the corresponding bond eigenfunction to the eigenfunctions occurring earlier in the table.

It is not as simple to compute the matrix components between these eigenfunctions as it was for the bond eigenfunctions themselves. It was found best to express these eigenfunctions in terms of the Slater eigenfunctions and compute the matrix elements from the rules for forming matrix components between the Slater eigenfunctions. The results are shown in Table IV. In the calculation of these matrix elements each eigenfunction was multiplied by the arbitrary factor $1/(2)^{\frac{1}{2}}$.

The greatest advantage gained by the orthogonalization comes from the fact that in symmetrical configurations and also some configurations in which some of the interchange integrals can be neglected a proper assignment of letters to the atoms will give a secular equation which may immediately be factored into smaller determinants. A brief inspection of the various possibilities is usually sufficient to determine the correct assignment of the letters in these cases. It is, of course, always convenient to make as many matrix components zero as possible and important that the maximum number of these fall in a particular row or column. Having done this, three evaluations of the determinant for proper choices of E ordinarily suffice to estimate the lowest root of the equation.

Not every choice of fourteen independent bond eigenfunctions would lead to orthogonal eigenfunctions which have as simple matrix components as the set chosen here. To secure simplicity each bond eigenfunction should differ from the others as little as possible without losing independence.

The seven electron problem is, of course, simply a special case of the eight-electron problem in which one of the electrons is at infinity. This amounts simply to setting equal to zero all the integrals containing one particular letter, say h.

The problem still remains: to what systems do these simplified calculations apply? At present this question seems best answered by a detailed application to a variety of cases. One of these cases we have already referred to and others are being investigated. In any case it seems logical to consider first the approximations given here, since the results may readily be extended to include the neglected multiple interchange integrals and orthogonality integrals should this be found desirable.

The Problem of Atomic Polarization

CHARLES P. SMYTH, *Frick Chemical Laboratory, Princeton University*

(Received January 28, 1933)

New values of atomic polarizations are obtained from the temperature variation of the dielectric constants of gases. Although the values are of a greater magnitude than those calculated for simple molecules from infrared intensity measurements, they show that the improbably high values previously found for several alkyl halides are incorrect. If the molecule is not very large, its atomic polarization is a relatively small quantity unless dipole rotation may occur within the molecule as indicated by the dielectric constant of the substance in the solid state.

INTRODUCTION

IN an earlier paper[1] the writer collected the available data on atomic polarization and attempted to investigate such relations as might be found among them, a summary of this treatment being published subsequently.[2] At that time Van Vleck[3] had calculated from infrared intensity measurements that the vibrational or atomic polarization was negligibly small for HCl, HBr, CO, CO_2, NH_3 and CH_4 and attributed to experimental error the small but not inconsiderable values found for them, indicating, however, that this did not necessarily mean that other kinds of molecules might not possess significant atomic polarizations. In a recent treatment of these simple molecules,[4] he expresses scepticism as to "whether any information about the order of magnitude of the atomic polarization can be deduced from existing absorption data" and submits as "perhaps the best appraisal . . . that the effect of the atomic polarization on the dielectric constant is negligible in stable diatomic molecules, but not necessarily in molecules with more than two atoms." Smallwood[5] has recently attempted to calculate atomic polarizations but has obtained values much smaller than the observed. Thus far we have failed to account in a general quantitative fashion for the atomic polarization. The present paper offers new and, for the most part, more accurate data on atomic polarization, which will be used to answer certain newly arisen questions and to eliminate certain incomprehensibly large values from among the earlier data.

CALCULATION OF RESULTS

It will be remembered that the atomic polarization P_A is obtained by subtracting the electronic polarization P_E and the orientation or dipole polarization P_M from the total polarization $P=(\epsilon-1)M/(\epsilon+2)d$, in which ϵ is the dielectric constant, M, the molecular weight, and d, the density, that is, $P_A=P-P_E-P_M$. If P_M can be eliminated by fixing the dipoles in the solid state, P_A may be obtained by subtracting from P the value of P_E calculated by extrapolating the molar refraction to infinite wave-length. Some of the difficulties of this method have already been discussed and others which have been made evident by recent work on solids will be treated presently. Since, in the Debye equation, $P=a+b/T$, $a=P_E+P_A$, P_A can, perhaps best, be determined from a, which is obtained from the temperature variation of P. When the previous tabulation of values of P_A was made, few accurate measurements of the temperature variation of the dielectric constants of gases were available and the extreme inaccuracy of some was not fully recognized. Moreover, as the present work will show, the apparent temperature variation of the polarization in solution is sometimes misleading. As previously pointed out, the values of P_A are,

[1] C. P. Smyth, J. Am. Chem. Soc. **51**, 2051 (1929).

[2] C. P. Smyth, *Dielectric Constant and Molecular Structure*, p. 163, The Chemical Catalog Company, Inc., New York, 1931.

[3] J. H. Van Vleck, Phys. Rev. **30**, 31 (1927).

[4] J. H. Van Vleck, *Electric and Magnetic Susceptibilities*, p. 51, Oxford University Press, Oxford, 1932.

[5] H. M. Smallwood, Zeits. f. physik. Chemie [B] **19**, 242 (1932).

at best, inaccurate, since they are determined as small differences between relatively large quantities, all the errors of experiment and method being thus accumulated in them. The values in Table I, assembled by Dr. Kenneth B. McAlpine, have been calculated from the temperature variation of the dielectric constants of the substances in the vapor state, which seems to provide the most accurate method of determination. Some recent data are omitted as being less accurate. An accurate value for ethyl either is taken from the old tabulation for comparison with a newly determined value.

TABLE I.

Atomic polarizations			
Nitric oxide	0.4[a]	Methyl fluoride	2.4[c]
Nitrous oxide	0.4[e]	Methyl chloride	2.2[c]
Carbon disulfide	0.3[f]	Methyl bromide	1.2[c]
Propylene	0.6[d]	Methyl iodide	1.4[c]
Propane	0.3[d]		
Benzene	1.9[d]	Ethyl chloride	1.4[c]
Toluene	2.5[d]	Ethyl bromide	2.9[c]
n-Heptane	1.1[c]	Ethyl iodide	1.5[c]
Ethylene oxide	1.8[g]	$CHFCl_2$	0.9[b]
Ethyl ether	3.9[g]	CHF_2Cl	3.9[b]
	3.3[h]	CF_2Cl_2	4.1[b]
		$CFCl_3$	3.0[b]

[a] C. P. Smyth and K. B. McAlpine, J. Chem. Phys. **1**, 60 (1933).
[b] C. P. Smyth and K. B. McAlpine, ibid. **1**, 190 (1933).
[c] C. P. Smyth and K. B. McAlpine, unpublished measurements.
[d] K. B. McAlpine and C P. Smyth, J. Am. Chem. Soc. **55**, 453 (1933).
[e] C. H. Schwingel and J. W. Williams, Phys. Rev. **35**, 855 (1930).
[f] C. T. Zahn, ibid. **35**, 848 (1930).
[g] H. A. Stuart, Zeits. f. Physik **51**, 490 (1928).
[h] O. Fuchs, ibid. **63**, 824 (1930).

DISCUSSION OF RESULTS

The atomic polarizations for the small molecules in Table I are small but not the negligibly small values that would probably be calculated from infrared intensity measurements. Although they are hardly larger than the possible experimental error, it is important to note that no negative values have been obtained, nor have negative values been obtained from any dependable measurements. This shows that the magnitude of the atomic polarizations cannot be due to experimental error. In accordance with a previously noted tendency, propylene and toluene, which have small dipole moments, have larger atomic polarizations than the closely related molecules of propane and benzene, which have no moments. The values for benzene and heptane vapors differ by less than the experimental error from those previously found for the liquids.

In measurements upon solutions of polymethylene bromides,[6] the moments of which increase with rising temperature because of the potential energy between the two principal dipoles in each molecule, it was found that the values of P_A calculated from the apparent values obtained for the constant a of the Debye equation were very high, 60 in the case of pentamethylene bromide. As an increase of moment with rising temperature would reduce the slope of the $P-1/T$ curve and thus give too large a value of a and of P_A, the apparent high P_A values were regarded as practically meaningless. This suggested the possibility that the surprisingly high values of the atomic polarization found for a number of alkyl halides[1,7] from measurements on temperature variation of the polarization might be due to an increase in moment with rising temperature. Although not highly probable, it appeared possible that there might be sufficient stretching of the carbon-halogen bond with rising temperature to cause an appreciable lengthening of the dipole with consequent increase in moment. In order to investigate this possibility, the values for the methyl and ethyl halides in Table I were acquired. The probable error in these values appears to be somewhat less than 1. As there is no regular trend in the values, it appears probable that the true values lie between 1.5 and 2.0. The values for the four substituted methanes are about twice as great, with the exception of that for $CHFCl_2$, in which the error would seem to be abnormally large. Although these molecules have moments smaller than those of the methyl and ethyl halides, they contain three or four principal

[6] C. P. Smyth and S. E. Kamerling, J. Am. Chem. Soc. **53**, 2988 (1931).
[7] C. P. Smyth and H. E. Rogers, J. Am. Chem. Soc. **52**, 2227 (1930).
S. O. Morgan and H. H. Lowry, J. Phys. Chem. **34**, 2385 (1930).

dipoles instead of one. Their larger atomic polarizations are in accord with the previous observation[1] that the atomic polarization is greater, the greater the number of dipoles in the molecule, probably because of the bending or displacement of these dipoles within the molecule.

The value 2.2 for methyl chloride compares with the value 8.1 found by Morgan and Lowry in hexane solution, 1.3 in carbon tetrachloride solution and 8.1 in the solid state, the latter value falling to 2.0 as the temperature was lowered from $-100°$ to $-190°$. The value 1.2 for methyl bromide compares with 21.4 in hexane solution and 2.8 for the solid at $-100°$, decreasing to 0.8 at $-120°$. For methyl iodide, Table I gives 1.4 as compared to values of 15.5 in hexane solution and 0 in the solid state. For ethyl bromide vapor, the value is 2.9 and for the iodide 1.5 as compared to 11 found by Smyth and Morgan[8] for the former in hexane solution and 12.3 by Smyth and Stoops[9] for the latter in heptane solution. The low values of the atomic polarizations of the vapors, which are dependable and of the same magnitude as those found for the solids, show that there is no detectable change of moment in these molecules in the temperature region studied. The high values of the atomic polarizations found in the measurements upon solutions must be regarded as incorrect.

In the measurements upon solutions each value of P used to determine the constants a and b for a substance was obtained by extrapolating to zero concentration a curve in which the polarization of the substance P_2 was plotted against its mole fraction c_2 in a nonpolar solvent. As the solvent reduces the forces between the polar molecules which lower the observed polarization, the value found for P_2 increases with increasing dilution and the P_2-c_2 curve rises rapidly as zero concentration is approached. As rising temperature diminishes the intermolecular action, the curvature of the curves becomes less pronounced so that the extrapolation to zero concentration becomes more accurate, the higher the temperature. Since extremely dilute solutions were not used in these measurements on the alkyl halides and since the same general method of extrapolation was employed on every curve, it is probable that the extrapolated polarization values at the lower temperatures are too low and approach the correct values only at the higher temperatures. Such polarization values would give a $P-1/T$ curve of too small a slope and, consequently, too large a value of P_A just as in the case of a substance, the moment of which increased with rising temperature.

A very pronounced case of the effect of solvent upon intermolecular action is shown by measurements upon butyl alcohol in heptane, cyclohexane and benzene solution.[9] In benzene solution, the moments calculated at 10° intervals from 20° to 70° deviate little from a mean value 1.74×10^{-18}, which is but slightly higher than the value 1.66×10^{-18} determined for the vapor.[10] In the other two solvents, the polarizations in the dilute solutions increase with increasing temperature instead of falling off as required by the Debye equation. Smallwood[5] calculates from these results in heptane solution an apparent moment of 1.29×10^{-18} at 10° rising to 1.65×10^{-18} at 70° and seems to imply that the difference is due to the effect of the solvent upon the actual polarization of the alcohol molecule. Since, however, it is difficult to picture the change in the moment of the alcohol molecule as occurring with sufficient ease to be affected by the difference in solvent, it seems more reasonable to adhere to the view originally advanced by Smyth and Stoops that the benzene is more effective than the heptane and cyclohexane in reducing the forces between the alcohol molecules. On this view the extrapolated polarization of the alcohol in heptane solution is much lower than the true value for the molecules isolated from one another at the low temperatures and approaches the true values with rising temperature, being approximately correct at 70°. The failure of the solvent to eliminate the effect of the forces between the polar molecules at the lower temperatures is so considerable as to be obvious in the case of the heptane solutions of butyl alcohol. A much smaller failure in the case of the solvent in the alkyl halide solutions could cause the large values observed for the atomic polarizations.

[8] C. P. Smyth and S. O. Morgan, J. Am. Chem. Soc. 50, 1547 (1928).

[9] C. P. Smyth and W. N. Stoops, J. Am. Chem. Soc. 51, 3312 (1929).

[10] J. B. Miles, Phys. Rev. 34, 964 (1929).

Determinations on Solids

The highest atomic polarization seeming to possess any real significance thus far reported is the value 33.4 for dimethyl sulfate in the solid state.[11] Later measurements of the dielectric constant of solid dimethyl sulfate[12] give evidence of dipole orientation between the melting point, −31.4°, and a transition at −68.0−71.0°. If this is an orientation of dipoles within the molecule, as seems rather probable, the polarization arising from it must be classed as a true atomic polarization, which drops to a small value below the transition point. If, however, it arises from a limited orientation of the molecule as a whole, the atomic polarization must be estimated from the small dielectric constant below the transition point.

The high atomic polarization, 24.8, calculated by Ebert for cane sugar,[13] may arise from orientation of the hydroxyl group dipoles within the molecule but may be due, at least in part, to the presence of water in the material. The same may be said of Ebert's value 28.4 for citric acid containing a molecule of water of hydration, which probably contributes heavily to the value of P_A. In view of the rotation of the water molecule in ice and the great elevation of the dielectric constant by the presence of minute quantities of ionic impurities,[12] large values of P_A for solids liable to contain traces of water must be viewed with scepticism. As small quantities of impurities may cause the presence of liquid in the solid for some distance below the freezing point, it is evident that, unless the substance is very pure, the atomic polarization must be determined at temperatures far below the freezing point, although the use of high frequency in the dielectric constant measurements tends to reduce the effect of impurities.[12] In the case of small polar molecules, like those of water and the hydrogen halides, ordinarily high frequencies and low temperatures would be useless in determining P_A because of the rotation of the molecules in the space lattice. However, P_A may be determined for these small molecules from the temperature variations of the polarizations of the gases.

Conclusions

It may be concluded that improved methods of determining atomic polarization have demonstrated the incorrectness of the large values previously reported except, perhaps, in the case of complex molecules where dipole orientation may occur within the molecule. In the calculation of a large dipole moment, the error caused by neglect of atomic polarization is normally almost negligible.

[11] J. Errera, *Polarisation Diélectrique*, p. 115, Les Presses Universitaires de France, Paris, 1928.

[12] C. P. Smyth and C. S. Hitchcock, J. Am. Chem. Soc. **54**, 4631 (1932).

[13] L. Ebert, Zeits. f. physik. Chemie **114**, 430 (1925).

The Rate of Dissociation of Nitrogen Tetroxide[1]

CHARLES EDWIN TEETER, JR., *Research Laboratory of Inorganic Chemistry, Massachusetts Institute of Technology,* Department of Chemistry, University of California†*

(Received January 17, 1933)

It has long been supposed that the rate of dissociation of nitrogen tetroxide could be calculated from observations of the dispersion of the sound in the gas. Einstein's equations gave the velocity constant in terms of the dispersion and the properties of the substances, regarded as ideal, acoustically transparent gases. Dispersion has been reported and rate constants calculated by several observers. On the other hand an equal number of negative results have been reported. Recently the theory has been examined critically by D. G. C. Luck and modified to take account of the absorption of sound and the deviations from the gas laws. Moreover dispersion has been observed for nondissociating gases, particularly carbon dioxide. In this gas, time lag in the equilibrium between vibrational and translational-rotational degrees of freedom causes an increase of velocity exactly parallel with that caused by dissociation. Indeed any type of equilibrium in the system may be expected to produce a dispersion of sound in some frequency region related to its own frequency, and it is not possible to distinguish between the types of equilibrium by sound measurements. The use of very small measuring tubes also produces a dispersion of somewhat smaller magnitude. Under these circumstances it is difficult to see how any interpretation can be made or conclusions drawn. In a series of measurements made during the last five years, the author has found no measurable dispersion of sound in N_2O_4 up to 53.8 kc. The velocity of sound at this frequency agreed closely with that determined by Grüneisen and Goens at audible frequencies, although high absorption made observation difficult. At higher frequencies no evidence of transmission could be obtained although sound up to 860 kc was employed. This increasing absorption shows that we are entering a dispersive region but it is not possible to say whether dissociation, time lag, or a combination of both is responsible for the dispersion. This applies equally to the velocity increases found by Richards and Reid in the same frequency region. Hence it seems that the sonic method for measuring rates of dissociation is not likely to fulfill the hopes of its proponents, and further experimental work will not be fruitful.

I. THEORY OF THE CALCULATION OF THE RATE CONSTANT

The dispersion equations of Einstein

The speed at which the reaction $N_2O_4 \rightleftarrows 2NO_2$ attains equilibrium has been a subject of investigation for the last forty-seven years. Ordinary methods are useless for so rapid a reaction, and attempts have been made to determine the rate by measurements of the velocity of sound in the gas.

The theory upon which this work was based was proposed by Einstein[2] in 1920. Equations were derived for the propagation of sound of different frequencies in a system of ideal, acoustically transparent gases one of which was the dissociation product of the other. At either very high or very low frequencies the velocity of sound is given by an exact equation not involving either the frequency or the rate constant of dissociation. At frequencies of the order of magnitude of the dissociation frequency dispersion sets in, and the velocity is given by an approximate relation involving both the sound frequency and the rate constant. These equations are:

at low frequencies, $V_0=[(p/\rho)(1+A/B)]^{\frac{1}{2}}$ (1)

at high frequencies, $V_\infty=[(p/\rho)(1+R/\bar{C}_v)]^{\frac{1}{2}}$ (2)

and at intermediate frequencies, $\nu=\omega/2\pi$,

$$V_\nu=\left[\frac{p}{\rho}\left(1+\frac{k_1^2AB+\bar{C}_vR\omega^2}{k_1^2B^2+\bar{C}_v\omega^2}\right)\right]^{\frac{1}{2}}. \quad (3)$$

* Contribution No. 26.

† This investigation was suggested by A. R. Olson, and the early portion of the work was carried out at the University of California with his counsel and cooperation. The author is indebted to the Parker Fund of Harvard University for a Fellowship in 1927–8, and to the National Research Council for a National Research Fellowship in 1928–9.

[1] A preliminary notice of this communication has already appeared. (J. Am. Chem. Soc. **54**, 4111 (1932).)

[2] A. Einstein, Sitzungsber. d. Berl. Akad. 1920, 380.

By solving (3) for k_1 and substituting (1) and (2) for their values we can obtain

$$k_1=(2\pi\nu\overline{C}_v/B)[(V_\infty^2-V_\nu^2)/(V_\nu^2-V_0^2)]^{\frac{1}{2}}. \quad (4)$$

Applied to the N_2O_4 dissociation, p is the pressure, ρ the density, k_1 the rate constant of dissociation,

$$A=\left(\frac{2D}{T}-\overline{C}_v\right)\frac{1-\alpha}{1+\alpha}+R\frac{2-\alpha}{\alpha},$$

$$B=\frac{D^2}{RT^2}\frac{1-\alpha}{1+\alpha}+\overline{C}_v\frac{2-\alpha}{\alpha},$$

D is the heat of dissociation at constant volume, α the degree of dissociation, $\overline{C}_v$ is the weighted average of the heat capacities of N_2O_4 and NO_2, $\overline{C}_v=[C_v''(1-\alpha)+2\alpha C_v']/(1+\alpha)$, and R is the gas constant.

Several of the early experimenters[3, 4, 5, 6] thought they had reached the dispersive region at audible frequencies. From some measurements completed in 1929 the author[7] believed he had found dispersion at 51.7 kc. Richards and Reid[8] report that they have found measurable dispersion from 92 to 450 kc and calculate rate constants.

On the other hand Grüneisen and Goens[9] found no dispersion up to 15.6 kc. Kistiakowsky and Richards[10] extended this to 80 kc. In the present paper new experiments are described which show no measurable dispersion up to 53.8 kc, but do show the presence of strong absorption, increasing greatly up to 860 kc. This indicates the advent of dispersion, without affording quantitative evidence.

The dispersion equations of Luck

It seems a particularly bad approximation to apply the ideal gas laws to a system such as $N_2O_4-NO_2$, where both gases deviate from ideality, but one (N_2O_4) deviates much more than the other. It becomes important therefore to examine D. G. C. Luck's[11] modification of Einstein's theory to apply to real gases and at the same time to take account of sound absorption. Since no equation of state was known for the gas mixture, Luck used a functional form, $p=f(\rho, T, \alpha)$. Following the general method of Einstein, he obtained

$$\frac{V_\nu}{V_0}=\left[\frac{1+\epsilon^2X^2}{1+X^2}\right]^{\frac{1}{2}}\left(\frac{1+\theta^2}{(1-\theta^2)^{\frac{1}{2}}}\right) \quad \text{for velocity,} \quad (5)$$

and

$$\theta=\frac{\lambda}{2\pi l}=\left[1+\frac{(1+\epsilon^2X^2)^2}{(\epsilon^2-1)^2X^2}\right]^{\frac{1}{2}}-\frac{1+\epsilon^2X^2}{(\epsilon^2-1)X} \quad \text{for absorption.} \quad (6)$$

In these equations X (termed the relative frequency) $=2\pi\nu/bk_1$, $\epsilon=V_\infty/V_0$, $V_0=\partial p/\partial\rho(1+ga/b)$, $V_\infty=\partial p/\partial\rho(1+g)$,

$$a=\frac{2-\alpha}{\alpha}+(1-\alpha)\frac{\partial p/\partial\alpha}{\partial p/\partial\rho}\frac{\partial \ln K}{\partial T}+\frac{(1-\alpha)\rho^2C_v}{pM}\frac{\partial p/\partial\alpha}{\partial p/\partial T}-\frac{D}{C_v}\left(\frac{\partial \ln K}{\partial\rho}-\frac{1}{\rho}\right),$$

$$b=\frac{2-\alpha}{\alpha}+(1-\alpha)\frac{D}{C_v}\frac{\partial \ln K}{\partial T}, \qquad g=\frac{\partial p/\partial T}{\partial p/\partial\rho}\frac{Mp}{\rho^2C_v},$$

$C_v=(1-\alpha)C_v''+2\alpha C_v'=$ heat capacity/mole of mixture, $M=$ molecular weight, l is the distance in which the amplitude of the sound is reduced by

[3] E. and L. Natanson, Wied. Ann. **24**, 454 (1886); **27**, 606 (1886).

[4] Argo, J. Phys. Chem. **18**, 438 (1914).

[5] F. Keutel, Inaug. Diss., Berlin (1910).

[6] H. Selle, Zeits. f. physik. Chemie **104**, 1 (1923).

[7] A. R. Olson and C. E. Teeter, Jr., Nature **124**, 444 (1929).

[8] W. T. Richards and J. A. Reid, J. Chem. Phys. **1**, 114 (1933).

[9] E. Grüneisen and E. Goens, Ann. d. Physik **72**, 193 (1923).

[10] G. B. Kistiakowsky and W. T. Richards, J. Am. Chem. Soc. **52**, 4661 (1930).

[11] D. G. C. Luck, Phys. Rev. **40**, 440 (1932).

the factor e^{-1}, and K is the dissociation constant. The equations reduce to the form given by Einstein if the equation of state becomes $\rho/M \cdot RT(1+\alpha)$ and θ becomes negligible. By assuming values of ϵ, Luck is able to show the form of the velocity and absorption curves but application to the calculation of rate constants cannot as yet be made, since the differential coefficients, $[\partial p/\partial \rho]_{\alpha, T}$, $[\partial p/\partial T]_{\alpha, \rho}$, and $[\partial p/\partial \alpha]_{\rho, T}$ are at present unknown and not measurable, and there is no equation of state from which they may be computed. The curve for V_ν/V_0 differs in position but not in shape from that plotted from Einstein's equation. That for absorption rises rapidly in the dispersive region and attains a maximum at $X=1/\epsilon$, thereafter dropping off again.

If Luck's equations are solved for k_1 the relation

$$k_1{}^L=\frac{2\pi\nu}{b}\left[\frac{V_\infty{}^2(1+\theta^2)^2-V_\nu{}^2(1-\theta^2)}{V_\nu{}^2(1-\theta^2)-V_0{}^2(1+\theta^2)^2}\right]^{\frac{1}{2}} \text{ is obtained.}$$

This is seen to reduce to the form derived from Einstein's equations,

$$k_1{}^E=\frac{2\pi\nu\bar{C}_v}{B}\left[\frac{V_\infty{}^2-V_\nu{}^2}{V_\nu{}^2-V_0{}^2}\right]^{\frac{1}{2}} \text{ if the gases are ideal,}$$

and to the form $k_1{}^L=(2\pi\nu/b)\cdot(1+\theta)/(1-\theta)$ at the absorption maximum. If a value of ϵ is assumed, θ and V_ν/V_0 at the absorption maximum can be calculated, while b and $\bar{C}_v/B$ follow from the dissociation data. It is thus seen that a rough notion of the separate effects of the deviation from the gas laws and the absorption of sound can be obtained, if for K the variable $K_p=F(p, T, \alpha)$ is used. The chief uncertainties are in the values of ϵ, α, and $\partial K/\partial T$, in the case of ϵ since V_0 and V_∞ calculated from Luck's equations may not be the same as the values from Einstein's equations. At the absorption maximum $X=1/\epsilon$ and $\theta=(\epsilon-1)/(\epsilon+1)$. Also $V_\nu/V_0=(1+\epsilon)/2$ (approximately, if ϵ is near 1). Using values of V_0 and V_∞ calculated from Einstein's equations, we find that ϵ varies from about 1.04 to 1.06 at 25°. With $\epsilon=1.05$, $V_\nu/V_0=1.025$ and $\theta=0.024$. This means that the amplitude will be diminished $1/e$ in 6.6 wave-lengths. By substituting in the two equations for k_1, $k_1{}^L=2\pi\nu/b\times1.050$ and $k_1{}^E=2\pi\nu\bar{C}_v/B\times1.012$, a difference of about 3.8 percent. If $\epsilon=1.06$, $\theta=0.029$ and $k_1{}^L=2\pi\nu/b\times1.060$, $k_1{}^E=2\pi\nu\bar{C}_v/B\times1.015$, a slightly greater difference. The other factors b and $B/\bar{C}_v$ may be calculated to show the effect of the deviations from ideality. At 25° and 565 mm pressure $b=86.1$ and $b'=B/\bar{C}_v=77.5$, a difference of about 10 percent. At this same temperature and 260 mm $b=75.7$ and $b'=65.3$, and at 106 mm $b=58.1$ and $b'=49.9$, differences of roughly 14 and 13 percent, respectively. At lower temperatures the calculation becomes too uncertain as the values for α and K were experimentally determined[12] only at 25°, 35° and 45°.

Unfortunately no more information can be gleaned from Luck's equations in the present state of our knowledge. It might be possible to guess at the values of the constants for an equation of state, but the accuracy would not be sufficient to justify a calculation from Luck's equations. We may state, however, that at the absorption maximum the values of k_1 from Einstein's equations may be about 4 percent too low on account of absorption and perhaps 15 percent too high because of deviations from the gas laws.

The dispersion equations of Kneser

At the end of Luck's paper it was pointed out that dispersion due to other causes than dissociation might render invalid any conclusions drawn from acoustic data. Such dispersion was observed for air and carbon dioxide by Pierce[13] and Reid,[14] and it was attributed by Herzfeld and Rice[15] to a time lag in energy transfer from translational to internal molecular degrees of freedom. More lately Kneser[16] studied this dispersion both theoretically and experimentally, and found an effect closely analogous to and of nearly the same magnitude as that predicted by the Einstein theory for the dissociation dispersion. In CO_2 the velocity rose about 3.5 percent in the frequency

[12] F. H. Verhoek and F. Daniels, J. Am. Chem. Soc. **53**, 1250 (1931).

[13] G. W. Pierce, Proc. Am. Acad. Sci. **60**, 27 (1925).

[14] C. D. Reid, Phys. Rev. **35**, 814 (1930).

[15] K. F. Herzfeld and F. O. Rice, Phys. Rev. **31**, 691 (1928).

[16] H. O. Kneser, Ann. d. Physik (5) **11**, 761 (1931); **11**, 777 (1931).

region 100–600 kc and again became constant at higher frequencies. It is instructive to compare the equations Kneser derived for the velocity at different frequencies (which gave curves checking his data closely) with the corresponding equations of Einstein. For very low frequencies he found $V_0=[(p/\rho)(1+R/C)]^{\frac{1}{2}}$, and for very high frequencies, $V_\infty=[(p/\rho)(1+R/C_a)]^{\frac{1}{2}}$. For intermediate frequencies in the dispersive region he obtained

$$V_\nu=\left[\frac{p}{\rho}\left(1+R\frac{C+C_a\beta^2\omega^2}{C^2+C_a^2\beta^2\omega^2}\right)\right]^{\frac{1}{2}}. \qquad (7)$$

In these equations C is the total heat capacity per mole and C_a is the part of the heat capacity due to translational and rotational degrees of freedom. The symbol β represents the time characteristic of excitation of the vibrational degrees of freedom. If Kneser's equation for V_ν is rewritten

$$V_\nu=\left[\frac{p}{\rho}\left(1+\frac{RC+RC_a\beta^2\omega^2}{C^2+C_a^2\beta^2\omega^2}\right)\right]^{\frac{1}{2}}, \qquad (7')$$

and Einstein's equation is written

$$V_\nu=\left[\frac{p}{\rho}\left(1+\frac{AB+R\bar{C}k_1^{-2}\omega^2}{B^2+\bar{C}^2k_1^{-2}\omega^2}\right)\right]^{\frac{1}{2}}, \qquad (3')$$

the close similarity between the two dispersion formulas may be seen. By a fortunate choice of constants it would be possible to explain a given dispersion either as dissociation or as time lag.

It should be pointed out that Kneser, like Einstein, used the ideal gas laws and neglected sound absorption in his derivation. Hence his equations should be modified in the same way to take account of deviations from these ideals. This would not be expected to alter the similarity of the two corrected formulas.

It can be readily seen that any type of equilibrium in the system, whether in the intermolecular forces, in a chemical reaction, or in the states of the molecules themselves would be expected to give a dispersion in some frequency region related to its own frequency. If the dispersive regions overlap or coincide it is very difficult to see how any clear interpretation can be made or conclusions drawn.

The dispersion equations of Richards and Reid

Nevertheless an attempt has been made by Richards and Reid to modify the Einstein theory to include the "heat capacity" dispersion of Pierce, Reid and Kneser as well as the dissociation dispersion. The resulting equation however is used only to try to justify their neglect of the heat capacity effect. In their derivation, an absorption term is included, but this also is neglected in all calculations. The ideal gas laws are still assumed throughout. With this procedure the equation

$$V_\nu^2(1-\beta^2V_\nu^2/\omega^2)/(1+\beta^2V_\nu^2/\omega^2)^2=(p/\rho)\gamma \qquad (8)$$

is obtained. Here β, the "damping coefficient" used by Richards and Reid, is nearly identical with the "l" used in Luck's equations, and $\gamma(=C_p/C_v)$, which is also the ratio of isothermal to adiabatic compressibilities (Richards and Reid seem to have this ratio inverted), is given by a complex involving the different heat capacities, the frequency, and also the time lag θ (Kneser's β). When absorption and time lag are negligible (8) should reduce to the form given by Einstein. It is evident that there is an algebraic error in the reduction as carried out by Richards and Reid. Their Eq. (9) should read

$$k_1=\omega\left\{\frac{C_0RT^2\alpha[2+\alpha(1-\alpha)]}{(2-\alpha)[C_0RT^2(2+\alpha(1-\alpha))+D^2\alpha(1-\alpha)]}\right\}\left\{\frac{V_\infty^2-V_\nu^2}{V_\nu^2-V_0^2}\right\}^{\frac{1}{2}},$$

which readily reduces to our Eq. (4) above, instead of

$$k_1=\omega\left\{\frac{C_0RT^2\alpha[2+\alpha(1-\alpha)]}{(2-\alpha)[C_0RT^2+D^2\alpha(1-\alpha)]}\right\}\left\{\frac{V_\infty^2-V_\nu^2}{V_\nu^2-V_0^2}\right\}^{\frac{1}{2}},$$

which is used in all their calculations. Fortunately, this error is independent of frequency and affects only the first or smaller term of the denominator. The rate constants calculated in Tables VI

and VII, however, should be decreased by about 5 percent on this account.

The tube dispersion

A somewhat smaller change of velocity with frequency is caused, as has long been realized, by the use of very small tubes as the measuring chambers. The effect of small tubes is quite complicated. In the first place the close proximity to the walls causes side reflections which break up and distort the sound pattern and cause the appearance of spurious nodes and antinodes. If an attempt to avoid these disturbances is made by examining only the region close to the source of sound, the anomalies noted by Pierce and Reid are likely to vitiate the results. In the second place the velocity, according to the Helmholtz-Kirchhoff formula, will decrease as the sound frequency or the radius of the tube diminishes. In a region of dissociation dispersion this change of velocity would be expected to increase greatly as Richards and Reid pointed out. At the most they suggested that the correction might double. This will not be very significant if the dispersion observed is large and the tube dispersion only a small proportion of the total. However if the two are of nearly the same order of magnitude it becomes extremely important to know the tube dispersion very accurately in order that the corrected value for the dissociation dispersion may not be meaningless.

II. Experiments

Preliminary experiments

The apparatus was particularly designed to avoid the complications caused by the use of small tubes. Sound waves were produced in a chamber, made as large as possible to cut down wall effects, and standing waves were set up between the crystal which was the source of sound and a plane reflector. A sketch of the apparatus is given in Fig. 1 and a diagram of the electrical circuit in Fig. 2. The sound chamber was a bell of Pyrex tubing five inches in diameter, the open end of which was closed by a brass plate heavily coated with paraffin. The crystal, *c*, was contained in the male part of a $1\frac{1}{2}$ inch ground joint; the female part of which was sealed in a hole in the center of the brass plate. The lower electrode was a gold plate resting on a block of paraffin, the upper a square of platinum foil pressing lightly on the crystal. The seals *s*, *s* were made vacuum tight by applying beeswax and rosin and shellac on the outside. The reflector, *r*, was a lantern slide cover supported by a glass tube and moved by a calibrated screw *S*. A vacuum-tight movable joint, *j*, was made by stretching a piece of Gooch rubber tubing between rubber stoppers. To protect the rubber and to prevent it from collapsing under vacuum the tube was partly filled with a mixture of paraffin and vaseline. The chamber, itself thermostated, was in communication with a

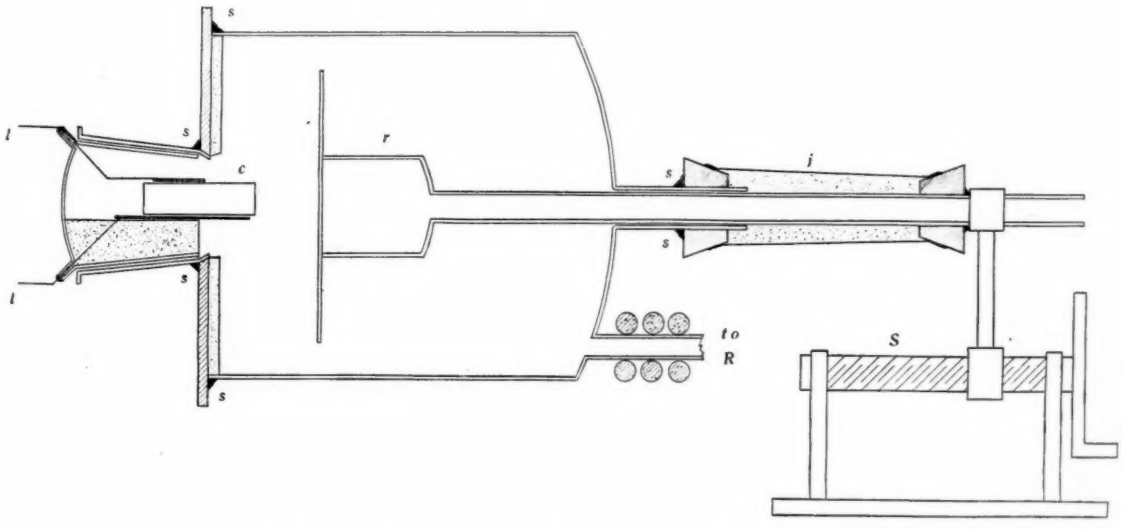

Fig. 1. Apparatus for measuring velocity of high-frequency sound in nitrogen tetroxide. Early form.

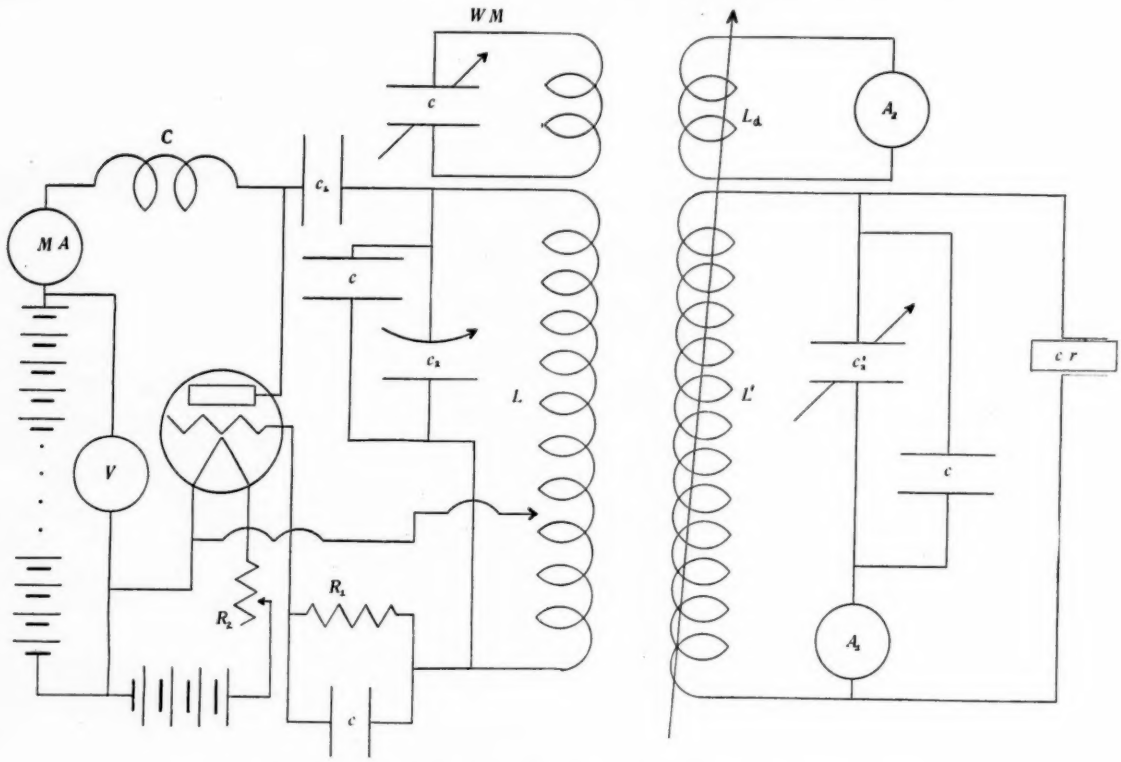

FIG. 2. Oscillating and resonance circuits for forcing vibration of quartz crystal.

reservoir of liquid nitrogen tetroxide at a definite temperature.

The quartz crystals were cut as suggested by Pierce. No success was had in inducing oscillation by means of his circuit, hence the power oscillator of Wood, Loomis and Hubbard[17] was employed. To the left of Fig. 2 is an ordinary Hartley oscillator and to the right a resonant circuit containing the crystal (*cr*). The inductances L, capacities c, choke C and resistances R have values determined by the tube and the crystal employed. In operation the Hartley oscillator was set to the frequency of the crystal with the aid of the standard wave meter, WM, the circuit $L'c_2'$ tuned to resonance with Lc_2 as indicated by the thermoammeter A_1, and the two circuits varied simultaneously until the crystal broke into oscillation. Moving the reflector had no effect on the plate meter of the Hartley oscillator (MA), but caused a regular rise and fall in the current indicated by the thermomilliammeter A_2 coupled to the resonance circuit through a small coil L_d. Other methods of detection were tried but none was completely satisfactory. The frequency was measured to about 0.2 percent by the standard wave meter. To check the apparatus the velocity of sound in air was measured. Erratic results were obtained very near the crystal, as was noted above, but at distances greater than three or four half wave-lengths the velocity was 332 m/sec. at 0° in close agreement with the accepted value. This figure was the mean of four series, comprising seventeen measurements in all.

The nitrogen tetroxide was prepared by heating a mixture of sand and lead nitrate previously dried at 120°. A strong current of oxygen—dry and free from CO_2—was passed through the combustion tube to minimize decomposition. The product was first collected in a trap cooled with solid CO_2-alcohol, then distilled through a column

[17] (a) Wood and Loomis, Phil. Mag. (VII) **4**, 417 (1927).
(b) Hubbard and Loomis, Nature **120**, 189 (1927).
(c) Hubbard and Loomis, Phil. Mag. (VII) **5**, 1177 (1928).
(d) Hubbard and Loomis, J. Opt. Soc. Amer. **17**, 295 (1928).

of P_2O_5, and finally collected in a bulb half filled with P_2O_5 and cooled in liquid air or CO_2-alcohol. The product obtained from distillation was pure white as a solid, and reddish brown as a liquid at the boiling point. Permanent gases were removed after the bulb had been sealed onto the main apparatus, first by pumping on the solid N_2O_4 with a mercury diffusion pump, and then by boiling off two liters of the gas into an evacuated flask with the temperature of the liquid about 0°. The residue was analyzed for air by sealing off a 50–100 cc bulb and noting the amount of undissolved gas after breaking the point of the bulb under KOH solution.

The reaction on the reflector fell off rapidly with distance from the crystal and only a few half wave-lengths could be measured. In the single successful series of measurements, the value 192.6 was obtained for the velocity of sound of frequency 51.7 kc in N_2O_4 at 25° and 565 mm. From this a rough value of the rate constant, $k_1=5600$ was calculated. Analyses showed 0.1 percent of air.

One of the chief criticisms of the early apparatus was the use of large surfaces of paraffin and vaseline. It was later shown that N_2O_4 exerts a slight but definite oxidizing action on these substances, NO and N_2O_3 being formed. This would tend to increase the velocity of sound. Another desirable modification was an increase of the sensitivity to permit measurements of a greater number of half wave-lengths and also greater distances from the crystal. It was also necessary to decrease the size of the reflector since at low frequencies large reflectors introduce periodic errors.

Final experiments

With all this in mind a new apparatus was built (see Fig. 3). The reflector was cut to $1\frac{1}{2}$ inches square. A new crystal holder was constructed of nichrome IV. Brass parts were triple gold plated and burnished. A groove was cut in the end plate, and the bottom of the Pyrex tube ground and polished to fit in this. The joint was made vacuum tight by filling the outside of the groove with a beeswax-rosin-ferric oxide mixture (at *s*, *s*). For the movable joint a metal stuffing box was used, sealed to the upper end of the chamber (*s*, *s*). A rod of nichrome IV supporting the plane glass reflector at one end passed through a well fitting nichrome bearing into the stuffing box. This was of steel, silver brazed to the bearing (at *a*, *a*), and contained a disk of talc turned and polished to a close fit, surmounted by a second disk of ceresin wax, and a third disk of Bakelite. Pressure was applied to the topmost disk by the threaded top which was also tubulated to act as a guide for the rod. Even under vacuum it was possible to advance or withdraw the rod without any leak. The rod was moved by a standardized screw (not shown).

The electrical circuit is shown in Fig. 4. The ordinary type of crystal controlled oscillator was employed. Values of L, C_1 and C_2 varied with the crystal used. To observe the change in the plate current as the reflector was moved, the bulk of the current was balanced out by the dry cell and the resistances R_3 and R_4. Only a small fraction of the current flowed through the Ayrton shunt AS to the galvanometer G. The latter had fifty divisions, each corresponding to 1.1 microampere. Although the amplitude of the sound must have been much less with this oscillator the reaction on the reflector in air was sufficient to produce full scale deflection of the galvanometer between nodes and antinodes.

No change was made in the method of making nitrogen tetroxide, as that was deemed satisfactory. The last experiment however was made with gas prepared by distilling C.P. red fuming nitric acid in a current of oxygen through a column of P_2O_5 and glass pearls and then through the apparatus previously used. It was found that practically all of the nitrogen tetroxide could be distilled off with the volatilization of only a small amount of nitric acid, and most of this was left in the first receiver. Further distillations under vacuum removed the remainder.

After distilling the nitrogen tetroxide into the main apparatus it was purified even more carefully than before. It was repeatedly distilled, frozen, left over P_2O_5, and pumped free of more volatile gases. After each experiment it was repurified, and before use analyzed for permanent gases and examined for N_2O_3 by condensation. A trace of the latter gas was sufficient to show a slight blue color against the pure white nitrogen tetroxide, especially as the trioxide condensed first.

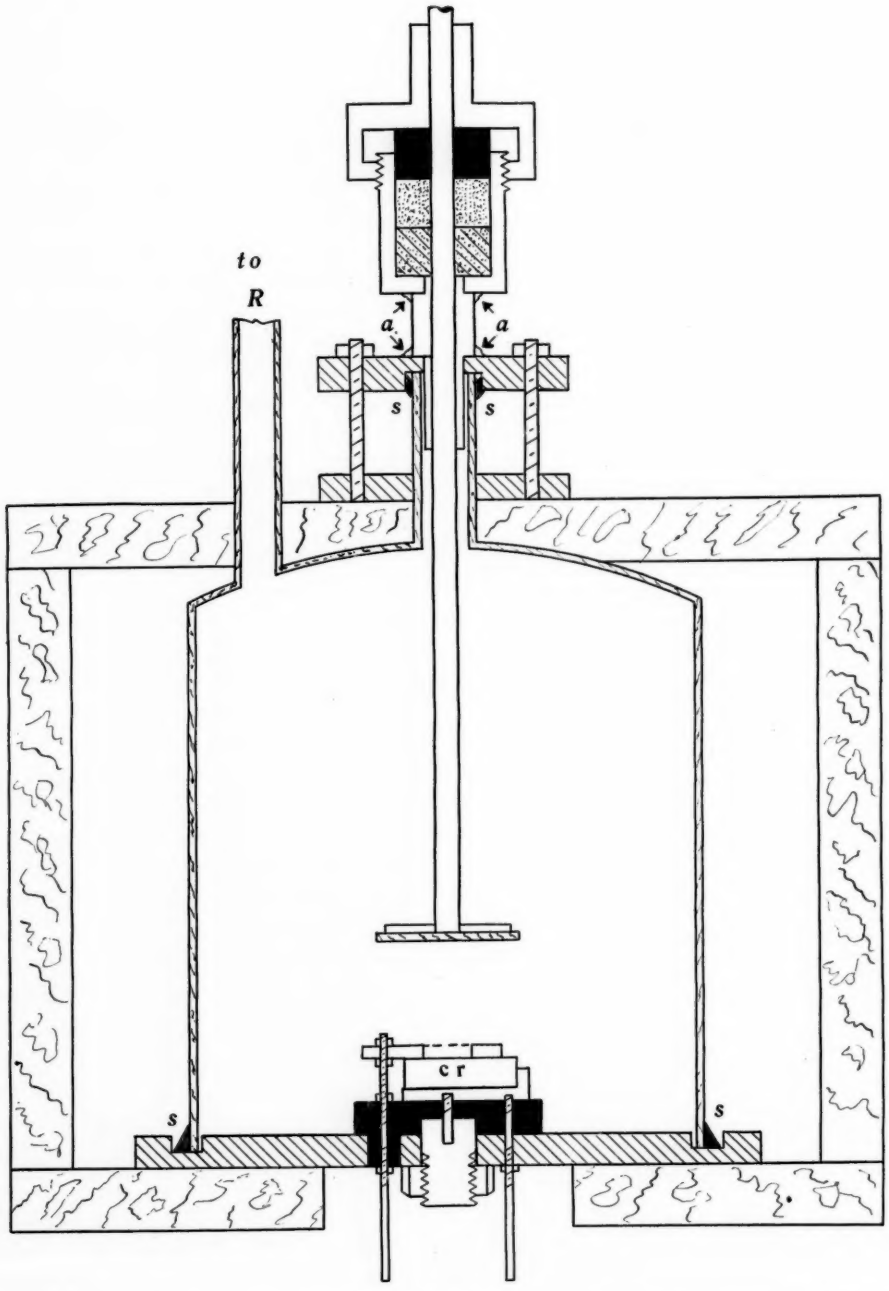

FIG. 3. Apparatus for measuring velocity of high-frequency sound in nitrogen tetroxide. Final form.

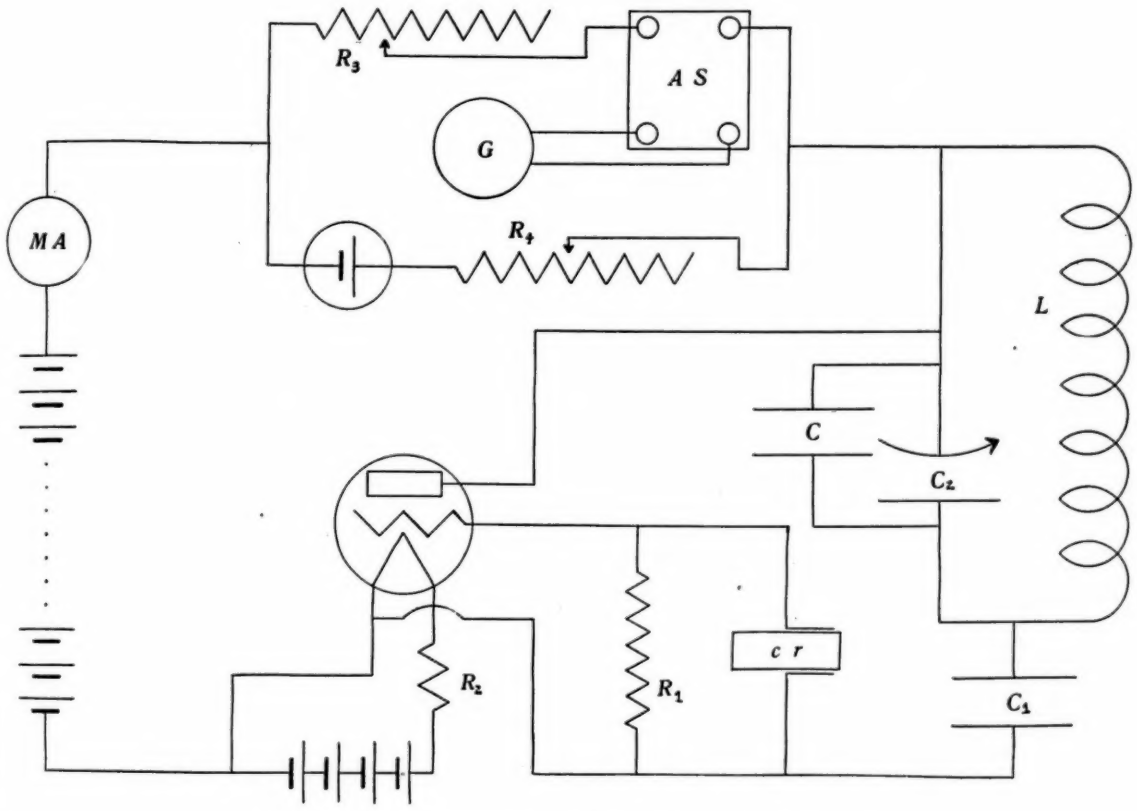

FIG. 4. Circuit of piezoelectric oscillator used in final experiments.

Three crystals were employed, approximate frequencies (to 0.2 percent) 53.8, 100.6, and 860 kc. These values were obtained by heterodyning the crystal oscillator with a second oscillator and measuring the frequency of the latter with a standard wave meter. More accurate measurements could easily have been made but were not deemed worth while. It should be noted that the frequency of a quartz crystal varies slightly with the temperature, and also changes with the mounting unless this is invariable.

The apparatus was checked by measurements in air at the two lower frequencies. At 53.8 kc and atmospheric pressure the velocity of sound, corrected to 0°, was found to be 333.0 m/sec. as the mean of 296 determinations of the half wavelength, $\lambda/2$. At 100.6 kc and atmospheric pressure the mean of 411 determinations gave 332.0 m/sec. for the velocity. Pierce obtained 332.4 m/sec. at 50 kc and 331.8 m/sec. at 100 kc. Reid found values for the velocity of sound which decreased with increasing distance from the source. At a mean distance of 15 cm the velocity was 332.7 m/sec. at 50 kc. At 30 cm it was 332.1 m/sec. and at 45 cm it was 331.8 m/sec. The mean distance in our experiment was about 10 cm so the high result is not surprising.

The results for nitrogen tetroxide are given in Tables I, II and III. The roman numerals represent different fillings of the chamber (new samples of nitrogen tetroxide); the Arabic numerals represent series of measurements on the same sample. In all the experiments except VI, Table I, from 3 to 5 stopcocks were in contact with the apparatus. All were lubricated with an "acid-proof" grease. In addition to these a mercury manometer was used intermittently to check the constancy of the pressure. This was disconnected whenever a reading was not being made. The actual pressure in the chamber, however, was determined from the vapor pressure curve of nitrogen tetroxide, which seems to be fairly well

known.[18] The amount of volatile decomposition product which reached the chamber during a run from these reactive parts of the apparatus must have been very small, as the amount of N_2O_3 produced on standing overnight was barely detectable. In the experiments reported the percentage of permanent gases was always below 0.3 percent, and no blue color of N_2O_3 could be observed on condensation. The stopcocks and manometer were used simply as a convenience and to save time. If positive results had been obtained no possible precautions would have been spared. As conclusive evidence that the presence of the stopcocks and manometer did not affect the velocity of sound, Experiment VI, (Table I) was made with a redesigned apparatus eliminating these reactive parts. The chamber and reservoir were separated by a thin glass partition which could be broken when desired. Provision was made for evacuating, filling and sealing off the reservoir, and for evacuating and sealing off the chamber separately. The wave-length found checked very well with the results of the other experiments, and the average velocity of sound obtained from all the measurements with the 53.8 kc crystal agreed with the low-frequency measurements of Grüneisen and Goens.[9]

In Experiment IV with the 53.8 kc crystal a rough determination of the absorption was made. It will be recalled that in air the reaction on the reflector caused a change of fifty scale divisions on the galvanometer between node and antinode, even at some distance from the crystal. In nitrogen tetroxide at a distance of less than $\frac{1}{4}$ inch from the crystal or only one $\lambda/2$ a change of less than fifteen divisions was observed. This fell off rapidly as the reflector was withdrawn from the crystal as shown in Table IV. In the space of some 6 inches or 45λ the reaction fell practically to zero.

At the higher frequencies no evidence of transmission could be obtained even very close to the crystal and although a range of pressures was explored. A reaction on the reflector of 0.5 scale divisions, or 1/100 of the effect in air, could easily have been detected. A confirmation that the absorption in N_2O_4 at 53.8 kc was much greater than that in air, the absorption at 100.6 greater than at 53.8 kc, and that at 860 kc greater than at 100.6 kc was the fact that at decreasing pressure limits for increasing frequencies enough

TABLE I. *Wave-length and velocity of sound in nitrogen tetroxide at 53.8 kc, 550 mm pressure, and 25°.*

Expt.	No. of check series	No. $\lambda/2$ measured	Av. $\lambda/2$ (scale divs.)
I	6	93	1.348
II	11	393	1.361
III	7	303	1.359
IV	5	317	1.364
V	3	114	1.354
VI	8	353	1.357
	Total	1220	Av. 1.360
Velocity of sound		186.9 m/sec.	

TABLE II. *Attempts to measure wave-length and velocity of sound in nitrogen tetroxide at 100.6 kc and various temperatures and pressures.*

Expt.	Temp. liquid	Press. (mm)	Temp. gas	Observations
		Series I		
I 1	−10.09	150	21.4	No transmission; crystal oscillated strongly.
2	− 3.65	216	21.5	
3	+ 0.07	265	21.2	
4	+ 5.01	343	21.2	
		Series II		
II 1	+ 4.71	338	19.8	No transmission; crystal oscillated strongly.
2	10.52	453	20.7	
3	15.03	565	20.3	No transmission; crystal oscillated feebly.
4	19.93	714	19.9	

At pressures greater than about 450 mm the crystal could not be made to oscillate strongly.

TABLE III. *Attempts to measure wave-length and velocity of sound in nitrogen tetroxide at 860 kc and various temperatures and pressures.*

Expt.	Press. (mm)	Temp. gas	Observations
	Series I		
I	97	25.0	No transmission; crystal oscillated strongly.
II	131	25.5	
	Series II		
III	123	25.0	No transmission; crystal oscillated strongly.
IV	78	25.0	

At pressures greater than about 140 mm the crystal could not be made to oscillate.

[18] (a) Scheffer and Treub, Zeits. f. physik. Chemie **81**, 308 (1912).

(b) Baume and Robert, Comptes Rendus **168**, 1199, 1201 (1919).

(c) Macisevskii, J. Russ. Phys. Chem. Soc. (Chemical Part) **48**, 1917 (1916).

(d) Mittasch, Kuss, and Schlueter, Zeits. f. anorg. Chemie **159**, 1 (1926).

TABLE IV. *Readings of screw, half wave-lengths, and change in galvanometer deflection in nitrogen tetroxide at 53.8 kc, 550 mm and 25.0°.*

Screw reading	Difference	No. λ/2	λ/2	Av. galv. defl. div.
		Series I		
28.95				
	13.20	10	1.32	14.8
42.15				
	16.51	12	1.37	13
58.66				
	12.59	9	1.40	10
71.25				
	10.53	8	1.32	7
81.78				
	9.47	7	1.35	5
91.25				
	11.50	8	1.44	3
102.75				
	10.56	8	1.32	2
113.31				
	12.04	9	1.34	1.5
125.35				
	19.74	15	1.32	0.5
145.09				
		Series II		
31.26				
	15.94	12	1.33	14
47.20				
	13.44	10	1.34	11
60.64				
	12.24	9	1.36	8
72.88				
	12.57	9	1.39	6.5
85.45				
	11.74	9	1.31	4
97.19				
	12.37	9	1.37	2.6
109.56				
	13.77	10	1.38	1.6
123.33				
	9.75	7	1.39	0.5
133.08				
	11.41	8	1.42	0.6
144.49				

energy was absorbed to stop or greatly diminish the oscillation of the crystal. These limits were 575 mm for the 53.8 kc crystal, 450 mm for the 100.6 kc crystal and about 140 mm for the 860 kc crystal. Of course it might have been possible to increase the sensitivity of detection or the amplitude of the sound waves, and hence force some of the sound through the gas. But with the present apparatus it seems to be clearly demonstrated that the absorption is too great to be neglected. Since greatly increasing absorption accompanies dispersion, as shown by the theory of Luck and the experiments of Kneser, it may be assumed that we are entering a dispersive region, but no clue is afforded as to the cause of the dispersion.

III. DISCUSSION

Kistiakowsky and Richards calculated theoretical values of V_0 and V_∞ to check against their experimental points. Unfortunately in making use of Einstein's equations for this calculation they failed to check his algebra and hence missed the slip in sign in the equation for V_0. Hence a new calculation was desirable. This is made in Table V for 25° and various pressures, and the

TABLE V. *Observed velocities of sound in nitrogen tetroxide at 25° and various pressures.*

p(mm)	u obs.(m/sec.)	p(mm)	u obs.(m/sec.)
Kistiakowsky and Richards		Natanson	
9.9 kc		617	187.2*
776	183.0	492	189.9*
761	183.8	231	197.3*
364	192.4	102	208.1*
270	197.0†	43.6	220.2*
41.6 kc		Nernst and Keutel	
760	183.6†	606	188.7
491	188.8	308	196.6*
275	195.5†	221	199.8*
146	203.0†	106	210.4*
80.3 kc		Argo	
760	183.5†	685	189.0*
486	189.4†	Grüneisen and Goens	
333	193.5	760	184.1
304	195.3	565	187.0
Teeter		440	189.6
53.8 kc		265	194.5*
550	186.9		
Richards and Reid			
9 kc	92 kc		
668	185.2	185.3	
260	195.1†	195.4	
162	202.0	202.5	

* Extrapolated over 1°–5°, using temperature coefficient of 0.95 m/sec./degree.

† Average values.

curves are plotted in Fig. 5. On this diagram are given all recorded points obtained at or near this temperature at all frequencies. In making the calculation, the new data of Verhoek and Daniels[12] were used. These authors give $D = 13{,}960$ cal./mole at constant volume[19] (not 14,600 as used by Richards and Reid) and they use the values $C_v''(N_2O_4) = 12.75$ and $C_v'(NO_2) = 6.8$. These are not very accurate but do not greatly affect the results. Verhoek and Daniels' data do not permit the ready calculation of either K or α at a given pressure. They give instead equations involving $C_{N_2O_4}^\circ = g/mv$, the

[19] F. H. Verhoek and F. Daniels, J. Am. Chem. Soc. 53, 1186 (1931).

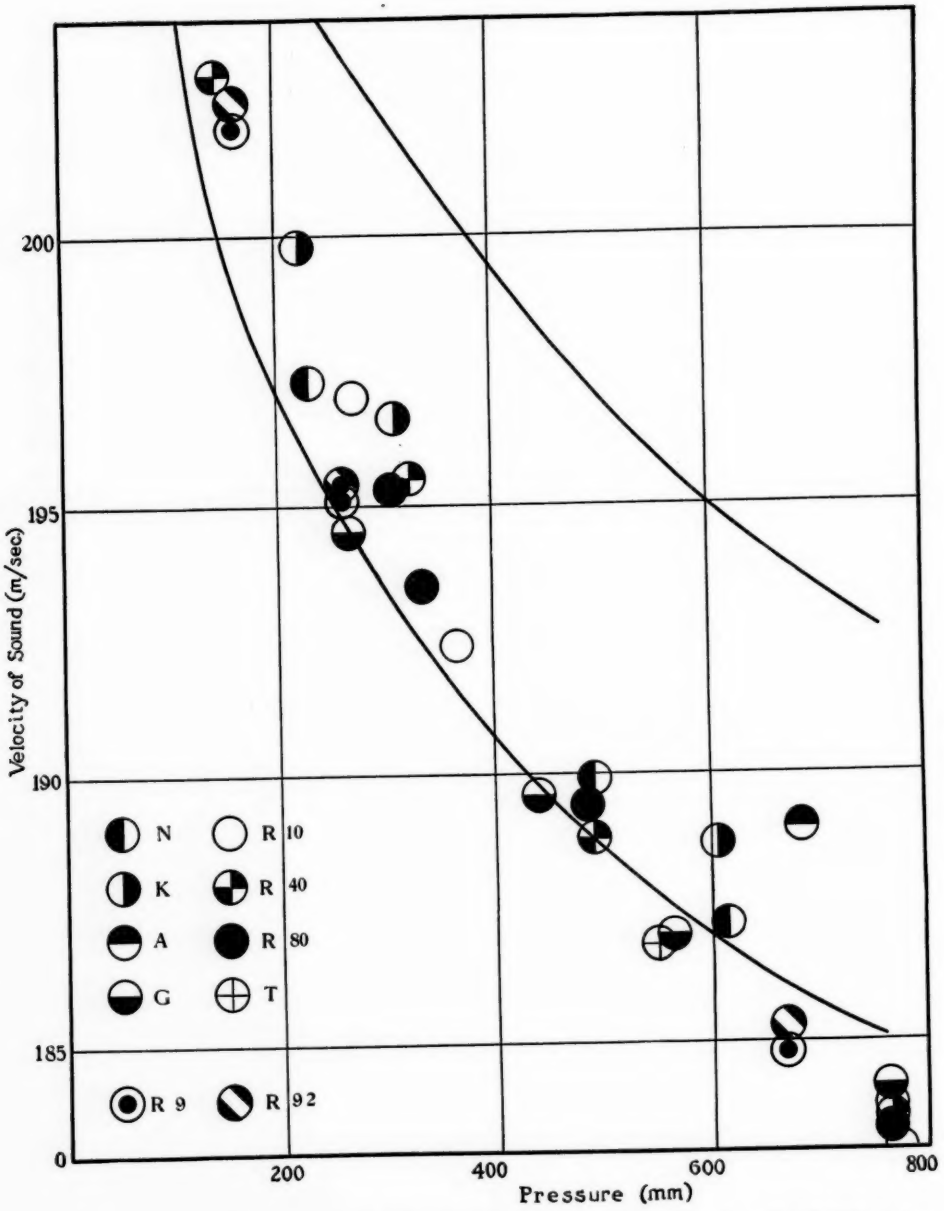

FIG. 5. Experimental and theoretical velocities of sound in nitrogen tetroxide at 20° and various pressures. Upper curve, values of u_∞, lower curve values of u_0, both calculated from Einstein's theory, by using Verhoek and Daniels' dissociation data. *N*, data of Natanson; *K*, Nernst and Keutel; *A*, Argo; *G*, Grüneisen and Goens; R10, R40, R80, data of Kistiakowsky and Richards at 10 kc, 40 kc, and 80 kc, respectively; *T*, Teeter, R9, R92 data of Richards and Reid at 9 kc, and 92 kc, respectively.

"concentration" of the gas, assumed all N_2O_4, in moles per liter. This may be expressed in terms of P, the total pressure in atmospheres, and α by the relation $\alpha=(P-p_{N_2O_4}^{\circ})/p_{N_2O_4}^{\circ}$, where $p_{N_2O_4}^{\circ}$ is the pressure which would be exerted by undissociated N_2O_4, which Verhoek and Daniels set equal to gRT/Mv. Here again we have the use of the ideal gas laws for N_2O_4, so that the resulting values for α will still be somewhat in error. However, assuming ideal conditions to apply, $C_{N_2O_4}^{\circ}=p_{N_2O_4}^{\circ}/RT=P/RT(1+\alpha)$. This gives two equations for K, $K=4\alpha^2P/(1-\alpha^2)$, and $K=a-bP/RT(1+\alpha)$, where a and b are empirical constants found from the experimental curves. Equating the two values of K and solving for α,

$$\alpha=\frac{bP/RT+[(bP/RT)^2+4(a+4P)(a-bP/RT)]^{\frac{1}{2}}}{2(a+4P)}.$$

The values of α thus calculated are always slightly lower than the corresponding values from previous calculations.

It should be noted that the points obtained by the authors, Grüneisen and Goens, and Richards and Reid, define a fairly smooth curve which crosses the experimental curve for u_0, deviations being negative at atmospheric pressure and becoming positive below 260 mm. Some of Kistiakowsky and Richards' points come fairly close to this experimental curve, but others as well as most of the early values lie above it. Exactly the same type of divergence between theory and experiment is seen in Richards and Reid's paper, Table V, where at constant pressure negative deviations of experiment from theory are found at 1°, and positive deviations at 30°. This type of behavior might be expected of an equilibrium mixture of two gases, one of which (N_2O_4) deviates much more from the ideal gas laws than the other.

This brings us to the paper of Richards and Reid. Are these authors really justified in neglecting absorption, deviation from the gas laws, and time lag? Are their values for the velocity constant really significant? Their arguments are complicated and not at all clear. Furthermore the confusion is increased by a number of errors throughout the paper. The algebraic mistake in their final equation has already been noted. In addition Tables III and IV giving the experimental values of the velocity of sound seem to be somewhat confused. All of the velocities are said to be "fully corrected," yet in the last three lines of Table III and all of Table IV it is not possible to obtain the sixth column ($V_\omega-V_0$) by subtracting the third column (V_0) from the fifth column (V_ω). If the sixth column be assumed correct (and if it is incorrect their whole argument falls) then a number of the values of V_0 have not been corrected. It also seems that values of $V_{451}-V_{94}$) have been labeled ($V_\omega-V_0$) and so used in the calculation whereas it is more logical to use values of ($V_{451}-V_9$) for the dispersion. The heat of dissociation at constant pressure was also used instead of that at constant volume.

Let us examine their arguments in order. To show that θ is negligible they first compare rate constants calculated from Eqs. (8) and (9). It is not clear just how Eq. (8) is used in this calculation, since this equation includes the effect of absorption as well as time lag. The magnitude of the former is entirely unknown and no mention is made of any assumption concerning it. From their calculations they conclude that if the constant k_1 calculated from experimental dispersions by (9) does not vary with frequency at frequencies greater than or equal to its own order of magnitude, the time lag can be completely neglected. They state, rather arbitrarily, that any dispersion as large as 1 m/sec. may be attributed at least in part to the dissociation. In order to establish further that θ may be neglected, they state the necessity of obtaining concordant values of k_1 at low frequency (and dispersion) and at higher frequency (and dispersion). The dispersion at the higher frequency must be "significantly greater than the maximum which can be produced by heat capacity change." What is this maximum? The maximum for CO_2 is about 9 m/sec. while the greatest dispersion observed by Richards and Reid for N_2O_4 was 5 m/sec. Furthermore a dispersion as great as 1 m/sec. is observed at 92 kc only at low temperatures (1°). The conclusion would seem to be that where absorption can be neglected, θ cannot be and *vice versa*. Richards and Reid next attempt to show that even small dispersions can be interpreted as wholly due to dissociation. Their argument is here particularly complicated and unconvincing,

but finally reduces to the agreement of values of k_1 at high and low frequency.

The apparatus used does not differ very greatly from that used by Kistiakowsky and Richards. An important exception is the use of 9 and 92 kc magnetostriction oscillators and dual reflectors in the same tube. This eliminates the difficulty of comparing different samples which accompanies the older method. At higher frequencies (94 and 451 kc) however separate tubes were used, and these were made still smaller. This brings us to the highly uncertain "tube correction." This was determined by measuring the difference for various gases between the 9 and 92 kc magnetostriction oscillators in 1 inch tubes and the 451 and 94 kc oscillators in 1 cm tubes. There is some question as to how the corrections of 0.4 and 0.8 m/sec. for the different tubes were calculated, and as to the justification of the assumption that no correction need be applied to the 92 kc oscillator in the 1 inch tube, and that -0.2 m/sec. is applied to the 451 kc oscillator in the 1 cm tube. The former is somewhat explained by the measured value of the velocity of sound in argon at 30° and 760 mm, 324.0 m/sec. "according well" with the value "324.2 calculated from data in *International Critical Tables*." The difference, however, is of the order of magnitude of the tube corrections (and of some of the dispersions observed). It should also be noted that in NO_2 the value of V_{94} in the 1 cm tube is about 0.6 m/sec. *less* than that of V_{92} in the 1 inch tube even after the corrections have been applied. Besides this there is the question, raised previously, of the increased tube correction in the dispersion region. This correction seems especially important for the calculation of the rate constants at 30° at 92 and 451 kc, for it is upon their equality that the whole argument depends. Different corrections at the two frequencies would throw the constants apart. The same applies to the correction for absorption which would increase as the absorption maximum is approached. A very rough calculation shows that the absorption maximum comes somewhere near 700 kc. Furthermore if the measured dispersion at 92 kc (0.2 m/sec.) is only 0.1 m/sec. too high (and all the velocities are accurate only to ± 0.1 m/sec. at best) the rate constant will be increased by nearly 50 percent.

The final argument for neglecting all the deviations from the simple theory is a comparison of observed velocities with those "calculated from (8) when absorption and time lag are negligible" and $\omega = 0$. This means the simple Einstein equations must have been used, although this is not pointed out. How good is the agreement? At higher pressures than 260 mm it is "unsatisfactory" and no data are given. At 260 mm and 30°, the only temperature for which data at 451 kc are available, the observed velocity of sound is about 2 m/sec. greater than the theoretical. At 1°C where dissociation is much less the observed velocity is about 1.1 m/sec. less than the theoretical. This latter value should be particularly noted as later Richards and Reid state that at 1°C, V_0 calculated from (9) agrees with the observed velocity at low frequencies within 0.1 m/sec. We have found (9) to be in error, but since this equation does not give directly a value of V_0, they may have used some intermediate equation, making a direct check on their statement difficult. However the values calculated from (8) in Table V seem to be free from error (cf. the value at 25°, 194.4, with that of u_0 in Fig. 5 of the present paper). In making the calculations Richards and Reid used interpolated experimental data of Verhoek and Daniels for the highest temperatures, but the figure at 1°C involves a long extrapolation of the dissociation constant and the use of the ideal gas laws. Richards and Reid consider the agreement between theory and experiment— $+2$ to -1.1 m/sec.—"sufficiently good" to base conclusions on dispersions of 0.2 to 1.8 m/sec. In view of the large discrepancies it seems rather questionable to use the measured rather than the calculated values of V_0 in Einstein's equations, or as a matter of fact to use these equations at all.

If Kneser's equations are solved for β^{-1} we obtain

$$\beta^{-1} = (2\pi\nu C_a/C)[(V_\infty^2 - V_\nu^2)/(V_\nu^2 - V_0^2)]^{\frac{1}{2}}.$$

Since C_a is wholly unknown it is not possible to carry out this calculation accurately. Making a rough guess at C_a and using Richards and Reid's dispersion data, β comes out about 5×10^{-5} at 92 and at 451 kc (Kneser found 1×10^{-5} for CO_2). It seems therefore that an intelligible re-

sult might be obtained by treating the dispersion as wholly due to time lag.

Another point which may be raised is the disagreement between the original results of Kistiakowsky and Richards over practically the same frequency range and the results of Richards and Reid. In the former no definite frequency trend in the region 10–80 kc was observed. At about 260 mm the velocity at 10 kc was nearly 2 m/sec. greater than that at 80 kc and that at 40 kc lay in between. Similar divergences were noted at other pressures. There is little difference apparent in the technique of the two series of measurements, but in the new series the tube correction of 0.4 m/sec. is applied. Application of this correction to the old results would not establish a definite frequency trend. It is difficult to see why the new measurements are so much better than the old, and Richards and Reid offer no explanation.

To sum up it seems that the interpretation of the measurements of the velocity of sound is not nearly as easy as at one time supposed. It seems hazardous to neglect any of the three disturbing factors—absorption, deviation from the ideal gas laws, and time lag in equilibrium between the degrees of freedom. Not only does it seem that the time lag should not be neglected but it also seems possible that it can account for all the results obtained so far by Kistiakowsky and Richards, Richards and Reid and the present author: all the velocity increases being anomalous dispersion due to the time lag and the high absorption that accompany the dispersion.

Allotropy of Liquid Nitrobenzene

EDMUND L. LIND AND T. FRASER YOUNG, *University of Chicago*

(Received January 30, 1932)

New measurements have been made of the surface tension and density of nitrobenzene between 6°C and 20°C. No evidence of allotropy was found. Neither intensive drying with phosphorus pentoxide nor the addition of moisture produced any anomalous density changes, although some samples, cooled from higher temperatures, were kept for twenty-four hours at 6°C.

RECENT work suggests that certain organic liquids may exist in two or more allotropic forms. Mazur,[1] and Wolfke and Mazur[2] report that the density, rate of cooling and dielectric constant of carbon disulfide, ethyl ether and nitrobenzene exhibit anomalous changes at various characteristic temperatures.

Menzies and Lacoss,[3] studying temperature plots of the specific volume, refractive index, pressure for melting, dielectric constant and specific heat of benzene, show that the smooth curves drawn by the various experimenters to represent their data might better be replaced by broken lines. These discontinuities are at about 40°C except in the pressure for melting. The vapor pressure and viscosity of benzene were found to exhibit similar irregularities.

Probably because of the magnitude and the convenient temperature (about 9.6°C) of the reported change for nitrobenzene, a number of workers have investigated this substance since Mazur's first notes appeared, and much contradictory evidence has resulted. Wolfke and Ziemecki[4] found that their plotted values of the index of refraction of nitrobenzene between the temperatures of 6.6°C and 14.6°C fell on a straight line. The discontinuity in their curve for molecular refraction arises from their use of Mazur's density data in their calculations. Friend[5] likewise failed to find evidence of a discontinuity in the index of refraction. Repeating Mazur's density work, he obtained a smooth curve, whereas there is a difference of more than 3 percent between Mazur's density measurement at 5.5°C and the value extrapolated from the high temperature portion of his curve. Friend's data of course led to a continuous function for molecular refraction. The density data of Tyrer[6] and of Massy, Warren and Wolfenden[7] are in agreement with those given by Friend.

Piekara,[8] in an investigation of the dielectric constant of carefully dried nitrobenzene, found no evidence of any transition above the freezing point, and further found that values for the super-cooled liquid fell on a curve continuous with that representing the data for temperatures above the freezing point.

Van Itterbeek,[9] using nitrobenzene furnished by the Bureau Internationale d'Etalons physico-chimique of Brussels, investigated the viscosity. His results are very interesting, since he reports no break in the temperature curve of intensively dried nitrobenzene, whereas he does find one at about 9.6°C for material not so dry. Massy, Warren and Wolfenden[7] found no discontinuity either in viscosity or in rate of cooling.

In investigations of the Raman spectrum for evidence of allotropy, neither Wolfke and

[1] J. Mazur, Nature **126**, 993 (1930); **127**, 741 (1931); **127**, 893 (1931); Comptes Rendus des Seances de la Soc. Pol. de Phys. **V**, 349 (1931); Acta Phys. Pol. **1**, 53 (1932).

[2] M. Wolfke and J. Mazur, Nature **128**, 584 (1931); Acta Phys. Pol. **1**, 71 (1932); Zeits. f. Physik **74**, 110 (1932).

[3] Menzies and Lacoss, Proc. Nat. Acad. Sci. **18**, 145 (1932).

[4] M. Wolfke and S. Ziemecki, Acta Phys. Pol. **1**, 271 (1932).

[5] J. N. Friend, Nature **129**, 471 (1932).

[6] D. Tyrer, J. Chem. Soc. **105**, 2534 (1914).

[7] N. B. Massy, F. L. Warren and J. H. Wolfenden, J. Chem. Soc. 1932, p. 91.

[8] A. Piekara, Nature **130**, 93 (1932).

[9] A. Van Itterbeek, Nature **130**, 399 (1932).

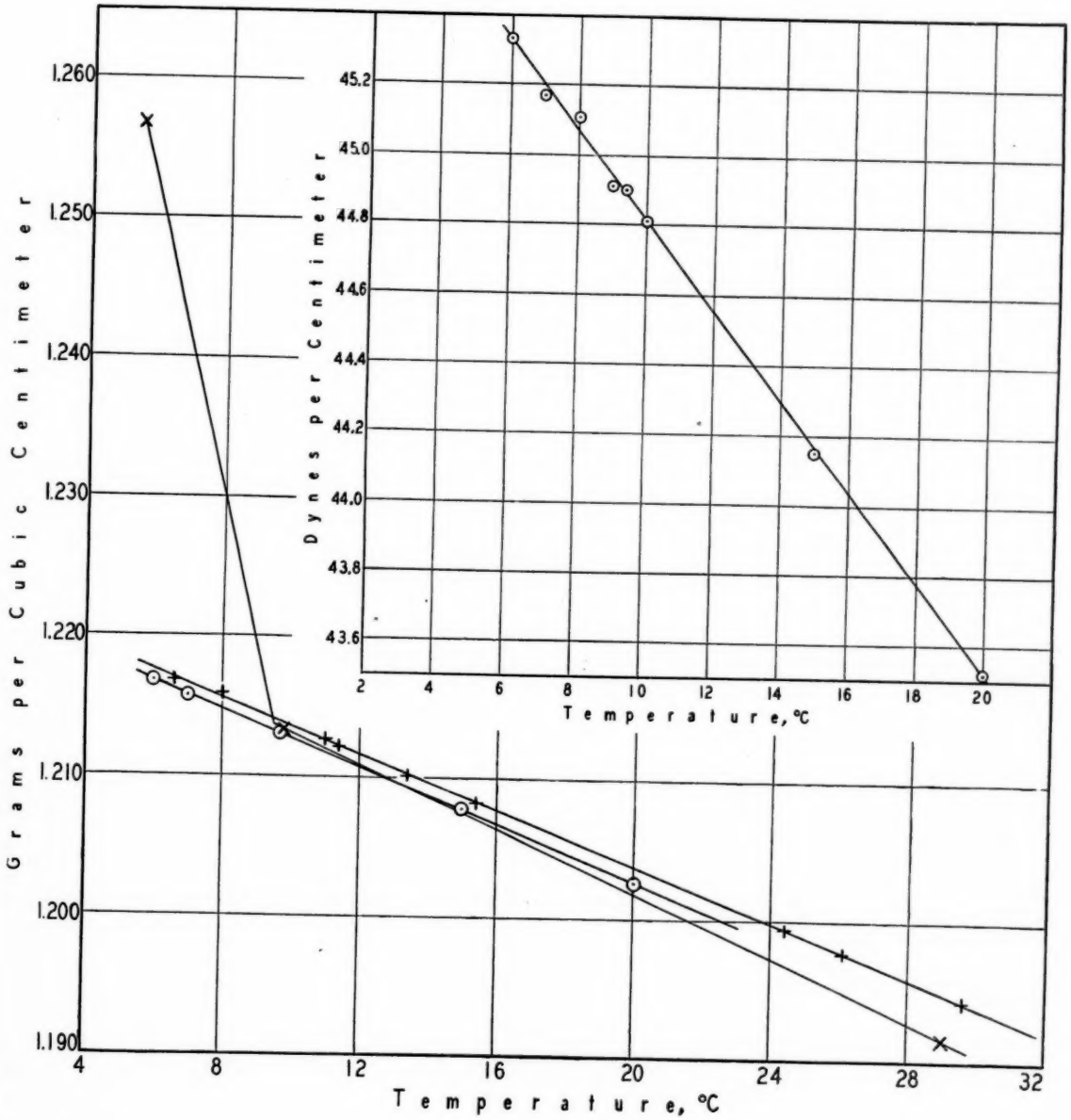

FIG. 1. Surface tension and density values. Mazur,* crosses; Friend, plus signs; Lind and Young, circles.

* Mazur, Nature **127**, 893 (1931); slightly different data are given in Acta Phys. Pol. **1**, 53 (1932).

Ziemecki[4] nor Thorne and Bayley[10] found any indications of a discontinuous variation with temperature. Stewart[11] reports that his x-ray diffraction measurements indicate "noticeable changes in the cybotactic groups" for nitrobenzene at 9.5°C, and rapid changes for ethyl ether at −105.4°C. The experiments which he reports, however, cannot confirm the existence of discontinuities characteristic of changes of state.

Allotropy of liquid nitrobenzene, whether due to changes in molecular aggregation or to other causes, would probably affect surface tension.

Measurements of this property in the neighborhood of 9.5°C seemed desirable to supplement the existing evidence for and against a transition at this temperature.

Experimental

A sample of Eastman's best grade of nitrobenzene was fractionated. A large portion was obtained which boiled within a range of 0.05°C at 211.$_4$°C, and froze within a range of 0.06°C at 5.5°C.

For the measurement of surface tension, a drop weight apparatus of the type described by Harkins and Brown,[12] Gans and Harkins,[13] and others, was adopted. The tip used was of Pyrex glass. Its diameter, as determined with a travelling microscope, was 0.4980 cm. The supply bottles were also made of Pyrex glass.

Fresh calcium chloride was kept in the drop weight box at all times, and any air entering due to temperature changes when the box was immersed in the thermostat, passed through a calcium chloride tube. Since much of the work was done at temperatures lower than that of the room, the box was not opened after removal from the thermostat until it had come to temperature equilibrium with the room. This was necessary in order to prevent the condensation of moisture upon the contents of the box. Thermostat temperatures, maintained constant to ±0.01°C, were determined to ±0.05°C.

For the determination of the factor[14] required for calculating surface tension from drop weights, the density is required. In order that our density data might be compared with those of Mazur and of Friend, they were determined carefully with a Pyrex glass pycnometer. Surface tension and density values are given in Table I, and are represented graphically in Fig. 1, together with the densities reported by Mazur and by Friend. Density values enclosed in parentheses were interpolated.

Table I.

Temperature	Density	Drop weight	Surface tension
6.0$_0$	1.2168	0.04369	45.33
7.0$_0$	1.2158	0.04353	45.17
8.0$_0$	(1.2148)	0.04347	45.11
9.0$_0$	(1.2138)	0.04327	44.91
9.4$_0$	(1.2134)	0.04326	44.90
9.7$_0$	1.2131	———	———
10.0$_0$	(1.2128)	0.04317	44.81
15.0$_0$	1.2078	0.04252	44.15
20.0$_0$	1.2025	0.04190	43.52

Density studies were continued as follows. Dilatometers were filled, one with nitrobenzene as used in our previous investigations, a second with slightly moist nitrobenzene, and a third with nitrobenzene intensively dried over phosphorus pentoxide; these were sealed and immersed in the thermostat. The last sample darkened somewhat on standing. Each sample contracted uniformly between 15°C and 6°C. Because of the possibility of a delayed transition, the dilatometers were kept at 6°C for twenty-four hours, but no further contraction in volume occurred.

Discussion of Results

It will be observed that our density curve differs but little from Friend's, and, like his, shows no such break as that of Mazur. Neither does the surface tension curve exhibit any irregularities (all points lie within less than 0.1 percent of the curve).[15] It must be recognized, of course,

[10] A. M. Thorne and P. L. Bayley, Phys. Rev. **41**, 376 (1932).

[11] G. W. Stewart, Phys. Rev. **39**, 176 (1932).

[12] W. D. Harkins and F. E. Brown, J. Am. Chem. Soc. **41**, 499 (1919).

[13] D. M. Gans and W. D. Harkins, J. Am. Chem. Soc. **52**, 2289 (1930).

[14] International Critical Tables, Vol. IV, p. 435, McGraw-Hill, New York (1928).

[15] Our value, 43.52 dyne/cm at 20°C, is in good agreement with the 43.38 of Harkins, Clark and Roberts,

that it is possible that our material lacked a catalyst necessary to produce transition from a metastable to a stable state, or that it contained an impurity sufficient to mask the effect, as suggested by Dobinski.[16] On the other hand, Mazur's liquid may have contained an impurity which produced a spurious effect[9] (possibly due to limited solubility). Further work is necessary to establish the existence or non-existence of discontinuities in any of the properties of pure liquid nitrobenzene. At the present time, it seems to us that there is a preponderance of evidence against the contentions of Mazur.

J. Am. Chem. Soc. **42**, 702 (1920), and the 43.35 reported by Hennaut-Roland and Lek, Bull. soc. chim. Belg. **40**, 177 (1931). The estimate in the International Critical Tables, Vol. IV, p. 454, for 20°C was based largely on less precise data, and now appears to be about 0.4 dyne/cm too high.

[16] S. Dobinski, Nature **130**, 662 (1932).

Dispersion and Polarizability and the van der Waals Potential in the Alkali Halides

JOSEPH E. MAYER, *Chemical Laboratory, Johns Hopkins University*

(Received January 26, 1933)

It is shown that the ultraviolet absorption of NaCl, KCl and KI, which one may estimate from recent experimental work, is in agreement with the dispersion of these salts. With these assumed absorption curves, the dipole-dipole potential constant for the van der Waals attraction between negative ions can be calculated with considerable accuracy. The constants can be estimated for the other alkali halides. The quadrupole-dipole constant is also approximated for all alkali halides. The resulting van der Waals potential is much greater than that previously calculated and accounts for the stability of CsCl type lattice for CsCl, CsBr and CsI. The polarizability of a given ion depends on the crystal. It is here assumed that the polarizability varies inversely as the "main frequency" in the crystal. This is shown to be in approximate agreement with experiment.

INTRODUCTION

LONDON[1] has shown that a dipole-dipole resonance potential varying as the inverse sixth power of the distance exists between all atoms and ions. An approximation formula was given by London for calculating the potential. Born and Mayer[2] have used this approximation to compute the van der Waals potential in alkali halide crystals. It was there remarked that the approximation used appeared to give considerably too small a value. Indeed, the existence of caesium chloride lattices leads to the conclusion that the actual van der Waals potential must be nearly twice that calculated. Recent unpublished investigations indicate that this potential is capable of quantitatively explaining the anomalous solubility and lattice constants of the silver halides, and that it is very large in these crystals.

It becomes of interest to investigate the possible methods of calculating the complete van der Waals potential in ionic crystals to ascertain if more reliable values can be obtained than those of Born and Mayer. Any such investigation must examine critically the values of the polarizabilities and absorption frequencies of ions in crystals. Furthermore, the dipole-quadrupole potential, inversely proportional to the eighth power of the distance, must be considered. Equations which may be used to evaluate this latter term have been obtained by Margenau.[3]

The approximation formula for the dipole-dipole potential most frequently used is, for two ions i and j at a distance apart r_{ij}

$$\Delta E_{dd} = -c_{ij}/r_{ij}^6; \quad c_{ij} \cong \tfrac{3}{2}(\epsilon_i\epsilon_j\alpha_i\alpha_j/\epsilon_i+\epsilon_j). \quad (1)$$

In this equation $\epsilon_i = h\nu_i$, $\epsilon_j = h\nu_j$ are energies corresponding to the "main frequencies" ν_i, ν_j of the ions i, j. α_i and α_j are respectively the polarizabilities of ion i and j. The equation is closely valid if absorption frequencies of considerable intensities are found only in the immediate neighborhood of the main frequencies. ϵ_i and ϵ_j are usually assumed to be, and are assumed by Born and Mayer to be, the ionization potentials of the ions. In the case of singly charged positive ions this is the second ionization potential of the element. In the case of negative ions it is the electron affinity.

The most obvious and serious objection to this use of the formula is that generally in crystals there is no absorption at all in the neighborhood of the assumed main frequencies of the negative ion. This paper shall be particularly concerned with the choice of values for ϵ and α in Eq. (1). A calculation of the potential constant c by means of a more accurate method is used to help in this choice and in the estimation of the error involved in the approximation. Furthermore, calculations are made of the dipole-quadrupole constant. In addition it is pointed out that estimates from experiment and theory of the relative absorption coefficients are in complete agreement with the dispersion data for some crystals. Some

[1] London, Zeits. f. physik. Chemie **B11**, 222 (1930).
[2] M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932).
[3] H. Margenau, Phys. Rev. **38**, 747 (1931).

proposals are made regarding the calculation of the polarizabilities of ions in crystals.

The Use of Absorption Frequencies

Experimental data

Pfund[4] has measured some reflection maxima in the region near 1600A for NaCl. Hilsch and Pohl[5] have carried out more extensive measurements of optical absorption down to 1600A for many alkali halides. The results are summarized in the latter of the two quoted articles. Hilsch[6] has used a most interesting method of electron collisions, by which he obtains curves which run parallel to the optical absorption over the range where this is known. Smith[7] has reported the absence of heavy absorption between the region investigated by Hilsch and by Hilsch and Pohl and a band at approximately 400A. Although this investigation was carried out only for NaCl the result may probably be safely generalized. It appears obvious, then, to associate the low-frequency band at approximately 1600A with the negative ion, and the one at around 400A with the positive ion. The excellent agreement between Hilsch's electron collision curves and the optical absorption for the range above 1600A may further incline one to assume that the optical absorption on the short wave-length side of this limit is approximately given by Hilsch's curves.

For several salts one may then assume an approximate experimental knowledge of the absorption between about 2500A and 1000A. To the high-frequency side of this region one may assume no or little absorption until approximately 400A, and there some sort of absorption due to the positive ion.

The assumptions are capable of fairly vigorous test in a few cases. The contribution of the positive ion to the dispersion curve can be estimated from the polarizability and frequency. In general the contribution is not large. The "frequency" of the positive ion may be assumed to be about that corresponding to its ionization potential in the gaseous state. It may more reasonably be expected to be somewhat lower, but even a considerable percentual difference in polarizability and frequency of the positive ion would not greatly affect the dispersion curve. It then remains to be seen if the experimental absorption in the 1600A region plus the small effect of the positive ion will account quantitatively for the known dispersion. Actually in only three cases are the complete data at hand. The dispersion has been measured for NaCl and KCl with great accuracy by Martens,[8] and good measurements by Gyulai[9] exist for KBr, NaBr, KJ, RbCl and LiF. Of these salts a considerable portion of the absorption is known optically only for KI. Hilsch's electron measurements show a sharply defined "absorption" which extends considerably farther into the ultraviolet. For NaCl and KCl satisfactory sharply defined curves are given by Hilsch, although only the long wave-length edge of the band has been optically measured.

For these three salts it is actually the case that analytical expressions which approximately agree with what is known of the absorption can be found, which also are in satisfactory agreement with the dispersion data. There appears to be no reason to doubt that exact agreement with the dispersion could be obtained without assuming an absorption in contradiction to the experimental values. Indeed such agreement can probably be found with so many different absorption functions that it appears to be of no value to continue further than has been done in this paper until more accurate experimental absorption curves far into the ultraviolet are at hand.

With a knowledge of the absorption curve, and of the dispersion (which latter is needed to fix the absolute value of the transition probabilities, since the absorption is measured in arbitrary units), one is in a position to make more exact calculation of the van der Waals potential between the negative ions in the crystals whose absorption is known. The relatively certain values so obtained can then be compared with the approximation formula (1) with a view to ascertaining the energies which one may best choose in such an equation.

[4] A. H. Pfund, Phys. Rev. **32**, 39 (1929).
[5] R. Hilsch and R. W. Pohl, Zeits. f. Physik **57**, 145 (1929) and **59**, 812 (1930).
[6] R. Hilsch, Zeits. f. Physik **77**, 427 (1932).
[7] A. Smith, Phys. Rev. **39**, 1013 (1932).
[8] F. F. Martens, Ann. d. Physik [4], **6**, 603 (1901); **8**, 459 (1902).
[9] Z. Gyulai, Zeits. f. Physik **46**, 80 (1928).

The exact equations

In crystals one has to deal with more or less continuous absorption. If we define as $q^2(\nu)$ the sum of all the amplitudes square up to the wave number ν, for one kind of ion in the crystal, say the negative,

$$q^2(\nu) = \sum_{k,\ \nu_{0k}=0}^{\nu_{0k}=\nu} q_{0k}q_{k0}, \tag{2}$$

then the derivative with respect to ν, $d[q^2(\nu)]/d\nu$ will be proportional to $q_{0k}q_{k0}$ at $\nu_{0k}=\nu$. The absorption coefficient at ν due to the negative ion, will be proportional to $\nu_{0k}q_{0k}q_{k0}$, that is, to $\nu d[q^2(\nu)]/d\nu$.

The following equations hold:

$$Q_{00}^2 = \int_0^\infty \frac{d[q^2(\nu)]}{d\nu}\,d\nu = \int_{\substack{\text{coordinate}\\ \text{space}}} \overline{\Psi}_0(\textstyle\sum q^2)\Psi_0 d\tau, \tag{3}$$

$$p = \frac{8\pi^2 mc}{3h}\int_0^\infty \nu \frac{d[q^2(\nu)]}{d\nu}\,d\nu = \textit{number of electrons}, \tag{4}$$

$$\alpha = \frac{2e^2}{3hc}\int_0^\infty \frac{1}{\nu}\frac{d[q^2(\nu)]}{d\nu}\,d\nu = \textit{polarizability} \tag{5}$$

$$c_{ij} = \frac{2e^4}{3hc}\int_0^\infty\int_0^\infty \frac{\{d[q^2(\nu_i)]/d\nu_i\}\{d[q^2(\nu_j)]/d\nu_j\}}{\nu_i+\nu_j}\,d\nu_i d\nu_j = \textit{dipole-dipole potential constant for like ions} \tag{6}$$

in which m is the mass of one electron and e its charge, h Planck's constant, and c the velocity of light. ν is wave number and has the dimensions cm^{-1}. Q_{00}^2 is the 00 matrix element of the sum of the coordinates squared for all electrons in the ion. In Eq. (6), were the constant c for unlike ions, it would be changed only by using two different functions $d[q^2(\nu)]/d\nu$.

If the integrations indicated are carried out from zero to infinity the equations are exact, providing the function $d[q^2(\nu)]/d\nu$ is exactly known. If the integrations are carried out only over the range of the ultraviolet where apparently almost all of the absorption due to the negative ion, except at x-ray frequencies, exists, a certain approximation is introduced. First obviously Q_{00}^2 will be the 00 matrix element of Σq^2 for at least only the outer electrons. Further a small proportion of the transitions of the outer electrons will be expected to be "double jumps" and will be far beyond in the ultraviolet. That is, Q_{00}^2 so calculated will be somewhat smaller than the $(\Sigma q^2)_{00}$ for all the outer electrons. The electron number p so calculated may be expected to be considerably smaller than the actual number of outer electrons since the small transition probabilities at high frequencies omitted become of considerable importance when multiplied by the wave number.

However the crystals are actually transparent for all frequencies below the range of consideration. Those functions, α and c_{ij}, as well as the dispersion, which have ν in the denominator will be given accurately in spite of the omission of some high-frequency transitions.

The dispersion due to the negative ion will be given by

$$D^*(\nu)_n = C\int_0^\infty \frac{\nu_i\{d[q^2(\nu_i)]/d\nu_i\}}{\nu_i^2-\nu^2}\,d\nu_i. \tag{7}$$

If however in this equation $D^*(\nu)_n$ is interpreted as being the additive contribution of the negative ion to the dispersion function $D(\nu)=(n^2-1)/(n^2+2)$, although an equation of the above form would be indicated, the frequencies would *not* be those experimentally observed in absorption. The function $D^*(\nu)=n^2-1$ will also be given by an equation of the form of (7) and here the frequencies will actually be the experimentally determined absorption frequencies, although the

constant C will not have a simple significance; that is n^2-1 is not additively composed of the contributions of each ion.[10] $D^*(\nu)_n$ is then to be compared to a function corresponding to n^2-1 due to the negative ion, which is obtained in the following manner.

$D(\nu)_p$, the contribution to $D(\nu)=(n^2-1)/(n^2+2)$ of the positive ion, is assumed to have the "single frequency" form $D(\nu)_p=a/(\nu_p^2-\nu^2)$. ν_p is taken as the frequency corresponding to the second ionization potential of the element. a is chosen to be in agreement with the polarizability of the positive ion, $Va/\nu_p=4\pi N\alpha/3$, with V the mol volume of the crystal and N Avogadro's number. The experimental $D(\nu)_n=D(\nu)-D(\nu)_p$ is then found, the contribution to $(n^2-1)/(n^2+2)$ of the negative ion, and from this $D^*(\nu)_n=3D(\nu)_n/(1-D(\nu)_n)$ is calculated, the value of n^2-1 if only the negative ions were present in the crystal. Since the absorption coefficient is only measured in arbitrary units, no attempt is made to define or determine further the constant C.

Calculations

It is now desired to select an analytical expression for $d[q^2(\nu)]/d\nu$ for which all the integrations can be conveniently performed, and such that $\nu d[q^2(\nu)]/d\nu$ is approximately equal to the experimentally determined absorption coefficient. The expression selected can be tested by comparison of $D^*(\nu)_n$ calculated from (7) with the "experimental" values obtained by the method of the preceding paragraph.

The expression $d[q^2(\nu)]/d\nu$ is assumed to be zero up to a certain wave number A, from A to increase linearly with ν to a maximum value b at $\nu=B$ (except that at $\nu=\nu_0$ lying near A it takes an additional value bf_0 due to a sharp line at ν_0), and then to decrease linearly with ν from $\nu=B$ to zero at $\nu=C$. From C to infinity it is assumed to be zero.

The absorption assumed is shown in Fig. 1 for NaCl, KCl and KI, along with what is known experimentally. The relative value of the intensity of the line at ν_0 is obtained by forcing the function to give the correct ratio to two extreme

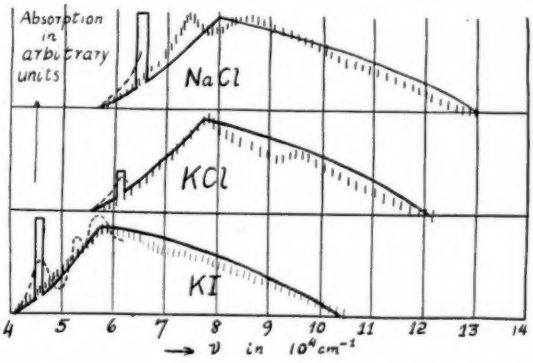

FIG. 1. Absorption curves for NaCl, KCl and KI. Unbroken curve, analytical expression; broken curve, optical absorption; curve with bars, electron collision method.

points on the dispersion curve. It is seen that this demand does not lead to an unreasonable value of the relative absorption at ν_0; indeed the complete omission of this line would change the results but little.

Using, then, this analytical expression

$$\begin{aligned} d[q^2(\nu)]/d\nu &= 0 \text{ from } \nu=0 \text{ to } \nu=A \\ &= [b/(B-A)](\nu-A) \\ &\qquad \text{from } \nu=A \text{ to } \nu=B \\ &= [b/(C-B)](C-\nu) \\ &\qquad \text{from } \nu=B \text{ to } \nu=C \\ &= 0 \text{ from } \nu=C \text{ to } \nu=\infty \end{aligned}$$

plus bf_0 at $\nu=\nu_0$, one obtains

$$\int_0^\infty \frac{d[q^2(\nu)]}{d\nu}\,d\nu = b[(C-A)/2+f_0]. \tag{3'}$$

$$\int_0^\infty \nu\frac{d[q^2(\nu)]}{d\nu}\,d\nu = \frac{b}{6}(C-A)(A+B+C), \tag{4'}$$

$$\int_0^\infty \frac{1}{\nu}\frac{d[q^2(\nu)]}{d\nu}\,d\nu = b\left[\frac{C}{C-B}\log\frac{C}{B}-\frac{A}{B-A}\log\frac{B}{A}+\frac{f_0}{\nu_0}\right]. \tag{5'}$$

[10] See K. F. Herzfeld and K. L. Wolf, Ann. d. Physik **78**, 35 (1925).

$$\int_0^\infty\int_0^\infty \frac{\{d[q^2(\nu_i)]/d\nu_i\}\{d[q^2(\nu_j)]/d\nu_j\}}{\nu_i+\nu_j}\,d\nu_i d\nu_j = b^2\Big\{\frac{f_0}{2\nu_0}+\frac{2f_0}{(C-B)(B-A)}[(C-B)(A+\nu_0)\log(A+\nu_0)$$
$$+(A-C)(B+\nu_0)\log(B+\nu_0)+(B-A)(C+\nu_0)\log(C+\nu_0)]$$
$$+[1/6(C-B)^2(B-A)^2][(C-B)^2(2A)^3\log 2A+(A-C)^2(2B)^3\log 2B$$
$$+(B-A)^2(2C)^3\log 2C+2(B-A)(A-C)(B+C)^3\log(C+B)$$
$$+2(C-B)(B-A)(A+C)^3\log(A+C)+2(C-B)(A-C)(A+B)^3\log(A+B)]\Big\}, \quad (6')$$

$$\int_0^\infty \frac{\nu_i\{d[q^2(\nu_i)]/d\nu_i\}}{\nu_i^2-\nu^2}\,d\nu_i = \frac{b}{2}\Big\{\frac{1}{C-B}\Big[(C+\nu)\log\frac{(C+\nu)}{(B+\nu)}+(C-\nu)\log\frac{(C-\nu)}{(B-\nu)}\Big]$$
$$-\frac{1}{B-A}\Big[(A+\nu)\log\frac{(B+\nu)}{(A+\nu)}+(A-\nu)\log\frac{(B-\nu)}{(A-\nu)}\Big]+\frac{2\nu_0 f_0}{\nu_0^2-\nu^2}\Big\}. \quad (7')$$

The actual magnitude of the absorption, the value of b, is determined by the experimental value of the polarizability. With the definition of $D(\nu)_n$ as the contribution of the negative ion to $(n^2-1)/(n^2+2)$, the polarizability of the negative ion,

$$\alpha_n = (3/4\pi N)\cdot V\cdot D(\nu)_n \quad (\text{at } \nu=0). \quad (8)$$

In Table I are all assumed and calculated values. The constant f_0 is determined from the ratio of $D^*(\nu)_n$ at the highest and lowest frequencies, and the undefined constant C in Eq. (7) from the value of $D^*(\nu)_n$ at one of these frequencies. The value of $D^*(\nu)_n$ calculated for an arbitrary frequency in the middle of the experimental range is compared with the experimental value

TABLE I.

	Salt			NaCl	KCl	KI
1	Assumed characteristic wave numbers of the amplitude—squared function	$A\times10^4$	cm^{-1}	5.70	5.56	4.17
2		$B\times10^4$	cm^{-1}	8.00	7.71	5.74
3		$C\times10^4$	cm^{-1}	13.00	12.17	10.45
4		$\nu_0\times10^4$	cm^{-1}	6.45	6.15	4.555
5	f_0 (calculated from the ratio of (10) to (14)		cm^{-1}	1370	274	960
6	$b\times10^{20}$ (calculated from X_n)		cm^3	0.895	1.06	1.69
7	$\alpha_{pos.}\times10^{24}$ (Pauling)[16]		cm^3	0.182	0.844	0.844
8	$\nu_p \times10^4$ (from ionization potential)		cm^{-1}	38.2	25.7	25.7
9	$\alpha_{neg.}\times10^{24}$ (from exp. dispersion)		cm^3	3.09	3.30	6.57
10	$D^*(\nu)_n$ experimental			2.411	1.830	2.602
11	at λ in A			1854	1854	2540
12	$D^*(\nu)_n$ experimental			1.720	1.245	1.914
13	at λ in A			2312	2312	3130
14	$D^*(\nu)_n$ experimental			1.268	0.901	1.460
15	at λ in A			6563	6563	6150
16	$D^*(\nu)_n$ calculated			1.708	1.258	1.910
17	at λ in A			2312	2312	3130
18	$Q_{00}^2\times10^{16}$		cm^2	3.40	3.54	5.46
19	p (electron number of neg. ion)			3.25	3.24	4.00
20	$c\times10^{60}$ (dipole-dipole constant for like neg. ions)			117	131	400
21	$\epsilon_c\times10^{12}$ ergs/molecule			16.4	16.1	12.3
22	ν_c		cm^{-1}	8.34	8.20	6.30
23	ratio ν_c/ν_0			1.29	1.33	1.38

(see rows 12 and 16). The agreement in all cases is within 0.3 percent in n, not, it is true, within the experimental error in n, but well within the expected error of the assumptions. It appears useless to attempt more complicated assumptions about the form of the absorption to get better agreement until more extensive experimental data are at hand.

The electron number of the chloride ion in NaCl and KCl have the same value, not however the value found by Herzfeld and Wolf[11] for the corresponding rare gas atom Ar, $p=4.61$, calculated by a similar method from the dispersion curve for the gas. The value found here for iodine, 4.00, is likewise not in agreement with their value 5.61 for Xe. Furthermore if the electron number of the positive ions is calculated from the polarizability, assuming a single main frequency at or near the ionization value, a poor approximation but the only available one, values much higher than those of the corresponding rare gases are obtained. It appears then inadvisable to assume a constant electron number value for a given configuration.

In row 21 and 22 are given values for ϵ_c and ν_c, the energy and corresponding wave number, which, with the experimental polarizability in the respective salts will give the values of c, the dipole-dipole potential constant, as calculated here, if inserted in Eq. (1). That is, Eq. (1) will give the correct constant c if the ϵ used is the ϵ_c of Table I. One of the main purposes of this paper is the determination of ϵ_c.

The determination of the frequencies

For the three salts, NaCl, KCl and KI, by means of exact equations, using assumptions which are unlikely to be in great error, the dipole-dipole potential constant has been calculated for the negative ions. By a correct choice of "main frequencies" the approximation Eq. (1) will give the same result. What are the corresponding frequencies in other salts?

To this problem it seems difficult to give a generally satisfactory answer. For the alkali halides the absorption frequencies observed appear to show sufficient empirical regularity to enable reliable guesses to be made. The obtaining of any sort of semi-theoretical basis which would enable extension to other salts is much more difficult.

Hilsch and Pohl have observed that the first pronounced absorption maxima at the long wavelength end agree well with the energy $\alpha e^2/r + J - E$. α is the Madelungs number, $\alpha e^2/r$ the electrostatic potential on one ion of the crystal, J the electron affinity of the negative ion, and E the (first) ionization potential of the metal. Born[12] has pointed out that this equation corresponds to the neutralization of two ions on the crystal surface, or on the surface of an interior split in the crystal. The corresponding $(2\alpha-1)e^2/r + J - E$ for the neutralization of two neighboring ions within the lattice[13] appears not to correspond to any intense absorption. The use of $\alpha e^2/r + J - V$ in which V represents the electron affinity of the crystal and may be calculated from magnetic susceptibilities has been suggested by Pauling.[14] The agreement is by no means convincing.

In Table II is given a list of the frequencies experimentally observed. A, the lowest frequency at which absorption appears, and ν_0 the first sharp line are taken from the optical data. The nomenclature is in agreement with the equation assumed previously for $d[q^2(\nu)]/d\nu$. B when bracketted is guessed at from the optical data, although it is never certain that the curve may not later rise; when not bracketted it is taken from Hilsch.[6] C is always taken from the data of Hilsch. In column 6 is given the value proposed for ϵ_c. For comparison $\alpha e^2/r$, J and E are given in columns 7, 8 and 9, and $\alpha e^2/r+J-E$ and $(2\alpha-1)e^2/r+J-E$ in columns 10 and 11, respectively.

Use of the ratio between ν_c and ν_0 found for the three salts and recorded in row 23 of Table I has been made in estimating ϵ_c. The values of ϵ_c may probably be relied upon to give the dipole-dipole constant for the potential varying as the inverse sixth power of the distance in Eq. (1) to within about 15 percent.

The positive ion frequencies are almost entirely unknown experimentally. The value of

[11] K. F. Herzfeld and K. L. Wolf, Ann. d. Physik **76**, 71 (1925).

[12] M. Born, Zeits. f. Physik **79**, 62 (1932).

[13] K. F. Herzfeld, *Handbuch der Experimentellen Physik*, Vol. VII, Part 2, "Gittertheorie."

[14] L. Pauling, Phys. Rev. **34**, 954 (1925).

TABLE II. *Frequencies of the alkali halides ergs/molecule* $\times 10^{12}$.

1	2	3	4	5	6	7	8	9	10	11
Salt	A	ν_0	B	C	ϵ_e	$\alpha e^2/r$	J	E	$(\alpha e^2/r)+J-E$	$(2\alpha-1)(e^2/r)+J-E$
LiF	(18.3)		23.2		24.3	19.81	6.58	8.55	17.84	26.31
Cl					17.5	15.51	5.97	"	12.93	19.56
Br	8.7	10.62			15.3	14.42	5.62	"	11.49	17.65
I	7.4	8.89	(11.69)		13.3	13.10	5.12	"	9.67	15.27
NaF		17.05	19.6	31.9	22.2	17.22	6.58	8.15	15.65	23.01
Cl	11.2	12.68	15.7	25.5	16.4	14.18	5.97	"	12.00	18.06
Br	9.2	10.33			14.5	13.39	5.62	"	10.86	16.58
I	7.4	8.56	(11.55)		12.8	12.35	5.12	"	9.32	14.60
KF					19.6	14.93	6.58	6.87	14.64	21.02
Cl	11.0	12.05	15.1	23.9	16.1	12.71	5.97	"	11.81	17.24
Br	9.4	10.46			14.2	12.11	5.62	"	10.86	16.04
I	8.2	8.96	11.25	20.5	12.3	11.30	5.12	"	9.55	14.38
RbF					18.5	14.14	6.58	6.62	14.10	20.14
Cl	10.68	11.76			15.7	12.20	5.97	"	11.55	16.77
Br	9.43	10.22			13.8	11.60	5.62	"	10.60	15.56
I	7.81	8.73	(10.42)		12.0	10.86	5.12	"	9.36	14.00
CsF					19.0	13.26	6.58	6.16	13.68	19.35
Cl	10.30	12.04			16.0	11.28	5.97	"	11.09	16.40
Br	9.32	10.52			13.9	10.81	5.62	"	10.27	14.95
I	7.63	8.96	(10.61)		12.1	10.19	5.12	"	9.15	13.56

about 400A given by Smith[7] for the NaCl crystal is some 65 percent of the series limit for the gaseous ion. One theoretical remark can be made, whereas removal of an electron from a negative ion neutralizes a lattice point and requires the work $\alpha e^2/r$, removal of an electron from a positive ion creates a doubly charged lattice point and releases the work $\alpha e^2/r$. Among the effects tending to raise the frequency of the negative ion to a higher value in the crystal than in the gas is probably a term $\alpha e^2/r$, this same term will probably tend to reduce the frequency of the positive ion in the crystal below the value in the gas. The relatively high frequencies of the positive ion will probably lead to a much smaller relative change in frequency with the change from gas to crystal, and a greater relative constancy of the frequency of one ion in different crystals.

POLARIZABILITIES

In the previous discussion it has been assumed that the polarizabilities of the positive ions are known, and are constants of the ion. The polarizabilities of the negative ions have been obtained by subtracting from the extrapolated value of $(n^2-1)/(n^2+2)$ at $\nu=0$ for the crystal, the contribution due to the positive ion. This method is justified only by the relatively smaller contribution of the positive ion and its probably smaller variation with the crystal than that of the negative ion.

Actually considerable doubt exists as to the values of the polarizabilities of the positive ions. Many measurements of the sum of the polarizabilities of positive and negative ions in solutions and crystals exist, and various estimates of the polarizabilities of the individual ions have been made. The values of Fajans and Joos[15] are doubtless quite good, and they have observed and remarked on the variation of these values with the state.

In this paper the polarizabilities calculated by Pauling[16] which are ostensibly those of the gaseous ions, are taken as fairly reliable average values for the positive ions in the crystals.

If Eqs. (3) and (5) are examined it is seen that, if the usual approximation of a single effective frequency is assumed, one may write

$$\alpha=(2e^2/3hc\nu)Q_{00}^2=(2e^2/3)(Q_{00}^2/\epsilon). \qquad (9)$$

In the three salts investigated, NaCl, KCl and Ki the correct ϵ to use in this approximation was found to be one to two percent higher than the ϵ_e

[15] K. Fajans and G. Joos, Zeits. f. Physik **23**, 1 (1924).
[16] L. Pauling, Proc. Roy. Soc. **A114**, 181 (1927).

to be used in Eq. (1). Herzfeld and Wolf[17] have used a similar approximation equation $\alpha = h^2e^2p/4\pi^2m\epsilon^2$, assuming the electron number p to be a constant for a given ion (indeed for a given configuration) and the polarizability α to vary inversely as the square of the main frequency. Although the excellent constancy of the electron number p for Cl^- in NaCl and KCl lends support to this view it appears to give too great a variation of α with the frequency in most salts. It seems reasonable however to assume that in Eq. (11) the Q_{00}^2, which represent a sort of size of the ion, will be unaffected by inclusion in a crystal, and will be a constant for any given ion. The polarizability would then vary inversely as the frequency. The frequencies of the positive ions are probably appreciably decreased from that of the gaseous state by inclusion in a crystal. The frequency in the crystalline state is however likely to be relatively independent of the crystal. For this reason the polarizability of the positive ion in the crystal is very probably fairly constant from crystal to crystal and somewhat higher than in the gaseous state. The values given by Pauling are probably better approximations for the polarizabilities in the crystalline state than in the gaseous.

Assuming that the polarizabilities of the positive ions are constant, and those given by Pauling, we may test the assumption that Q_{00}^2 is a constant for a given ion by calculating the extrapolated $(n^2-1)/(n^2+2)$ function at $\nu=0$ for all alkali halides, and comparing with the experimental values. A value of Q_{00}^2 for each negative ion is chosen so as to give the best average agreement. Table IV gives the results of such a calculation. The values of $(n^2-1)/(n^2+2)$ at $\nu=0$ are taken from Born and Heisenberg[18] and the experimental sum of the two polarizabilities calculated by means of Eq. (8). The values used for Q_{00}^2 are found in Table III. It is to be seen from Table IV that the agreement is not very good. Nevertheless deviations from pure additivity of the polarizabilities are between three and four times as great as those shown in Table IV. In view of the doubtful positive ion polarizability and the uncertain frequencies it is probable that better agreement could not be expected, even if the assumption were accurate. Better agreement could obviously have been obtained by assuming higher polarizabilities for the heavy positive ions, K^+, Rb^+ and Cs^+.

TABLE III.

Ion	F^-	Cl^-	Br^-	I^-
$Q_{00}^2\times10^{16}$	1.44	3.40	4.08	5.27

TABLE IV.

1	2	3	4	5	6	7
		Experimental			Calculated	
Salt	$\frac{n^2-1}{n^2+2}$	$\Sigma\alpha\times10^{24}$ cm³	$\alpha_{pos.}\times10^{24}$ cm³	$\alpha_{neg.}\times10^{24}$ cm³	$\Sigma\alpha\times10^{24}$ cm³	Diff. 3 and 6
LiF	0.234	0.906	0.030	0.90	0.93	+0.02
Cl	0.358	2.91		2.95	2.98	+ .07
Br	0.404	4.00		4.06	4.09	+ .09
I	0.450	5.93		6.00	6.03	+ .10
NaF	0.198	1.17	0.182	0.98	1.16	−0.01
Cl	0.306	3.27		3.14	3.32	+ .05
Br	0.346	4.38		4.29	4.47	+ .09
I	0.394	6.36		6.24	6.42	+ .06
KF	0.218	1.97	0.844	1.11	1.95	−0.02
Cl	0.280	4.14		3.20	4.04	− .10
Br	0.310	5.30		4.38	5.22	− .08
I	0.354	7.41		6.49	7.33	− .08
RbF	0.237	2.59	1.42	1.18	2.60	+0.01
Cl	0.282	4.71		3.29	4.71	− .00
Br	0.308	5.93		4.50	5.92	− .01
I	0.346	8.15		6.65	8.07	− .08
CsF	0.278	3.60	2.45	1.15	3.60	−0.00
Cl	0.244	5.70		3.22	5.67	− .03
Br	0.373	7.03		4.47	6.92	− .11
I	0.404	9.14		6.60	9.05	− .09

THE VAN DER WAALS POTENTIAL

It is now desirable to alter the approximation Eq. (1) used in calculating the dipole-dipole attractive potential to allow for the variable polarizability. An approximation equation is also desired for the quadrupole-dipole potential. These potentials are then calculated for the ions in the alkali halides.

Using Eqs. (1) and (9) one obtains:

$$\Delta E_{dd} = -(c_{ij}/r_{ij}^6); c_{ij} = \tfrac{2}{3}e^4(Q_{i00}^2Q_{j00}^2/\epsilon_i+\epsilon_j), \quad (10)$$

in which the Q_{i00}^2 is supposed to be a constant of the ion i and ϵ_i is dependent on the ion and on the crystal.

The values of ϵ for the negative ions are the ϵ_e values tabulated in Table II, column 6. For the positive ion a fair value is probably about $\epsilon=0.75\epsilon_0$ if ϵ_0 is the ionization potential of the gaseous ion.

[17] K. F. Herzfeld and K. L. Wolf, Ann. d. Physik **78**, 195 (1925).

[18] M. Born and W. Heisenberg, Zeits. f. Physik **23**, 407 (1924).

The complete potential in the crystal is

$$U_{dd}=-\frac{C}{r^6};\quad C=S_6'c_{+-}+S_6''\frac{c_{++}+c_{--}}{2},\qquad(11)$$

in which the sums S_6' and S_6'' are sums, respectively, over the odd and even lattice points of the crystal.[2] In Table V are tabulated the values

TABLE V. *van der Waals constants for the alkali halides.*

Salt	$C\times10^{60}$, ergs·cm^6				$d\times10^{76}$, ergs·cm^6			
	c_{++}	c_{--}	c_{+-}	C	d_{++}	d_{--}	d_{+-}	D
LiF	0.073	14.5	0.8	18.	0.03	17.	0.6	11.
Cl		111.	2.0	113.		223.	2.4	104.
Br		185.	2.5	183.		423.	3.3	190.
I		378.	3.3	363.		1060.	5.3	470.
NaF	1.68	16.5	4.5	46.	0.8	20.	3.8	31.
Cl		116.	11.2	180.		233.	13.9	180.
Br		196.	14.0	271.		450.	19.	300.
I		392.	19.1	482.		1100.	31.	630.
KF	24.3	18.6	19.5	167.	24.	22.	21.	150.
Cl		124.5	48.	452.		250.	73.	560.
Br		206.	60.	605.		470.	99.	800.
Cl		403.	82.	924.		1130.	156.	1420.
RbF	59.4	18.9	31.	278.	82.	23.	40.	290.
Cl		130.	79.	691.		260.	134.	960.
Br		215.	99.	898.		490.	180.	1340.
I		428.	135.	1330.		1200.	280.	2240.
CsF	152.	19.1	52.	495.	278.	23.	78.	600.
Cl		129.	129.	1530.		260.	250.	2600.
Br		214.	163.	2070.		490.	340.	3600.
I		424.	224.	2970.		1190.	520.	5800.

of c_{+-}, the potential constant for a single positive and a single negative ion, c_{++} the potential constant for two positive ions, and c_{--} that for two negative ions. C for the crystal is also tabulated.

Margenau[3] has calculated the quadrupole-dipole and quadrupole-quadrupole potentials, proportional to the inverse eighth and tenth powers of the distance, respectively, for like atoms. The equations can be easily generalized for unlike atoms or ions, i and j. The quadrupole-quadrupole term when evaluated is found to be altogether negligible and will not be here treated.

The approximation corresponding to Eq. (10) for the quadrupole-dipole potential between i and j at a distance apart r_{ij} is given by

$$\Delta E_{qd}=-d_{ij}/r_{ij}^8;$$

$$d_{ij}=e^4\frac{1}{\epsilon_i+\epsilon_j}[Q_{i00}^2Q_{j00}^4+Q_i^4Q_{j00}^2].\qquad(12)$$

The energies ϵ_i and ϵ_j in Eq. (12) are not necessarily the same as in Eq. (10), the correct averages which should be used as probably somewhat higher than those to be used in Eq. (10). Nevertheless for the purpose of the present approximation it will be assumed that they are the same. Q_{00}^4 is, analogously to Q_{00}^2, the 00 matrix element of the sum of q^4 for all electrons. The following equations are then nonrigorous, but will hold approximately:

$$Q_{00}^2=\sum_{\substack{\text{all}\\ \text{electrons}}}q_{00}^2=pq_{00}^2,\qquad(13)$$

$$Q_{00}^4=\sum_{\substack{\text{all}\\ \text{electrons}}}q_{00}^4=pq_{00}^4,\qquad(14)$$

$$q_{00}^4\leqq(q_{00}^2)^2,\qquad(15)$$

$$Q_{00}^4\leqq(1/p)(Q_{00}^2)^2,\qquad(16)$$

in which p is the number of electrons. Eq. (12) may then be rewritten,

$$d_{ij}=\tfrac{3}{2}c_{ij}(Q_{i00}^2/p_i+Q_{j00}^2/p_j).\qquad(17)$$

For p the geometrical mean of the electron number calculated from the polarizability and the frequency, and theoretical number of outer electrons (8 or 2) is taken. The complete quadrupole-dipole potential in a crystal becomes

$$U_{qd}=-D/r^8;$$
$$D=S_8'd_{+-}+S_8''(d_{++}+d_{--}/2).\qquad(18)$$

The values of d_{+-}, d_{++} and d_{--} as well as D are tabulated in Table V. The values of the sums S_6', S_6'', S_8' and S_8'' for both sodium chloride and caesium chloride type lattices are given in Table VI. The arithmetical values of the sums

TABLE VI.

Lattice type	NaCl	CsCl
S_6'	6.5952	8.7088
S_6''	1.8067	3.5445
S_8'	6.1457	8.2077
S_8''	0.8002	2.1476

given correspond to the use of the shortest lattice distance, the distance between unlike neighboring ions, for the r of Eqs. (11) and (18).

The values of the constants d and D are, of course, highly uncertain. They may be in error by as much as 50 percent of their value. However, no more accurate method of estimation appears to be available at present. The total quadrupole-dipole potential in the alkali halide

crystals, D/r^8, is in all cases between 10 percent and 20 percent of the dipole-dipole potential C/r^6. Since this latter term is itself in the nature of a small correction to the electrostatic attractive potential, the error introduced in calculations of the total potential by uncertainties in D is small.

A comparison of the values for CsI here calculated, $C=2970\times10^{-60}$ erg$\times$cm^6 plus $D/r^2=370\times10^{-60}$, giving 3340×10^{-60} with the value $C=1740\times10^{60}$ used by Born and Mayer is interesting. The newly computed values are fully capable of explaining the stability of the caesium chloride type lattice for CsI, CsBr and CsCl.

The author is greatly indebted to Professors Max Born and K. F. Herzfeld who have both helped greatly in developing some of the ideas expressed here.

The Calculation of Matrix Elements for Lewis Electronic Structures of Molecules

LINUS PAULING, *California Institute of Technology*

(Received February 14, 1933)

Starting from the discovery by Rumer that the eigenfunctions corresponding to different distributions of valence bonds in a molecule can be represented by plane diagrams which provide information regarding their mutual linear independence, a very simple graphical method is developed for calculating the coefficients of the integrals occurring in the matrix elements involved in Slater's treatment of the electronic structure of molecules.

IN his valuable paper[1] on *Molecular Energy Levels and Valence Bonds* Slater developed a method for formulating approximate eigenfunctions for molecules and for constructing the corresponding secular equation. This method has been successfully applied by a number of investigators in the discussion of general valence theory and of the structure of individual simple molecules, its application to more complex molecules having been retarded in part by the laborious nature of the calculation of the coefficients of the various exchange integrals in the matrix elements. It is shown in the following paragraphs that these coefficients can be easily calculated by a simple procedure involving the use of plane diagrams similar to those introduced by Rumer[2] in his recent discussion of the linear independence of electronic structures.

SINGLET STATES WITH SPIN DEGENERACY ONLY

For a system involving N electrons, Slater constructed the function

$$\Psi=\frac{1}{(N!)^{\frac{1}{2}}}\sum_{P''}(-1)^{P''}P''A(1)B(2)\cdots E(N),$$

which is completely antisymmetric in the electrons (satisfying Pauli's principle). Here A, $B\cdots E$ are one-electron spin-orbit functions, and the symbol P'' represents the $N!$ permutations of the functions $A\cdots E$ among the electrons, the coefficient being -1 for odd, $+1$ for even permutations. For two such functions Ψ and Ψ' the matrix element corresponding to a dynamical quantity F is

$$(1/N!)\int\{\sum_{P''}(-1)^{P''}P''A(1)\cdots E(N)\}F\{\sum_{P'}(-1)^{P'}P'A'(1)\cdots E'(N)\}dv,$$

which reduces to

$$\int A(1)\cdots E(N)F\{\sum_{P}(-1)^{P}PA'(1)\cdots E'(N)\}dv,$$

with $P'=P''P$, in case that F is completely symmetric in the electrons. This may be written as

$$\sum_{P}(-1)^{P}(AB\cdots E/F/PA'B'\cdots E'),$$

in which each parenthesis $(A\cdots E/F/PA'\cdots E')$ represents one integral in the above sum. If F does not involve spin interactions, the integral $(A\cdots E/F/A'\cdots E')$ vanishes unless the spin of A is the same as that of A', B as B', and so on, in which case it reduces to $(ab\cdots e/F/a'b'\cdots e')$, with $a\cdots e'$ the orbital parts of $A\cdots E'$.

For four electrons, for example, with only spin degeneracy (the number of occupied orbits equalling the number of electrons), Slater gave the function $\frac{1}{2}(\Psi_{\mathrm{I}}-\Psi_{\mathrm{II}}-\Psi_{\mathrm{III}}+\Psi_{\mathrm{IV}})$ as representing the structure in which orbits a and b are bonded together, and also c and d. Here $\Psi_{\mathrm{I}}\cdots\Psi_{\mathrm{IV}}$

[1] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

[2] G. Rumer, Nachr. d. Ges. d. Wiss. zu Göttingen, M. P. Klasse, p. 337 (1932).

are functions of the type given above with the following distributions of spins among the orbits:

	a	b	c	d
I	−	+	−	+
II	+	−	−	+
III	−	+	+	−
IV	+	−	+	−

The energy matrix element for this function is

$$(abcd/H/abcd)+(abcd/H/bacd)+(abcd/H/abdc)$$
$$-\tfrac{1}{2}(abcd/H/cbad)-\tfrac{1}{2}(abcd/H/dbca)$$
$$-\tfrac{1}{2}(abcd/H/acbd)-\tfrac{1}{2}(abcd/H/adcb)+\text{higher exchange integrals.}$$

With the single exchange integrals negative, as they usually are for orbits on separate atoms, this leads to attraction between a and b and between c and d, and repulsion between other pairs.

Similarly a function can be formulated representing $a-d$ and $b-c$ bonds, and one representing $a-c$ and $b-d$ bonds. These three functions, corresponding to three separate electronic structures of the Lewis type, are, however, not linearly independent; any one can be represented as a combination (sum or difference) of the other two. This linear dependence of structures continues as the number of bonds increases; for n single bonds between $2n$ atoms $(2n)!/2^n n!$ structures can be drawn, of which only $(2n)!/n!(n+1)!$ are independent. In the paper mentioned above, Rumer made the very interesting and important observation that if the orbits are formally arranged in a ring or other concave curve, and straight lines are drawn between orbits bonded together, the structures represented by diagrams in which no lines intersect are independent. This observation forms the starting point for the following treatment.

Let us arrange the orbits in a ring, and then draw arrows between pairs of orbits bonded together, the head of each arrow representing positive spin and the tail negative spin. The wave function for the corresponding structure is then given, except for a normalizing factor $2^{-n/2}$, by the sum of the functions corresponding to this distribution of spins and to those obtained by reversing the arrows, each function having the coefficient $(-1)^R$, in which R is the number of reversals. Thus the $\begin{smallmatrix}a-b\\c-d\end{smallmatrix}$ structure would be represented by the vector-bond diagram $\rightleftarrows$, corresponding to the function

$$\frac{1}{2}\left\{\begin{pmatrix}-&+\\+&-\end{pmatrix}-\begin{pmatrix}+&-\\+&-\end{pmatrix}-\begin{pmatrix}-&+\\-&+\end{pmatrix}+\begin{pmatrix}+&-\\-&+\end{pmatrix}\right\}.$$

It is verified at once that

$$\times = \downarrow\uparrow - \rightleftarrows,$$

so that an intersecting pair of arrows can be replaced by the difference of two non-intersecting pairs, the pair connecting head with head and tail with tail having the positive sign. By successive applications of this treatment any structure can be resolved into structures involving no intersecting bonds.

Canonical sets of independent structures

Of the various complete sets of independent structures which may be formulated, certain ones may be called "canonical" because of the relative simplicity of the calculation of matrix elements based on them. For a given order of the orbits in a ring, the canonical set of independent structures comprises those with no intersecting bonds; moreover, numbering the orbits in order about the ring, the canonical vector-bond structures for singlet states with spin degeneracy only have arrows drawn from odd to even orbits (the functions for the corresponding distributions of positive and negative spins thus occurring with the positive sign). The eigenfunction for a structure represented by a vector-bond diagram $a\rightarrow b$ $c\rightarrow d$, etc., may be written

$$\frac{1}{2^{n/2}}\sum_R(-1)^R R\left\{\frac{1}{((2n)!)^{\frac{1}{2}}}\sum_P(-1)^P Pa(1)\beta(1)b(2)\alpha(2)c(3)\beta(3)d(4)\alpha(4)\cdots\right\},$$

in which α represents positive spin and β negative spin, P represents the $(2n)!$ permutations of the orbits and their associated spins among the electrons, and R the 2^n operations of interchanging the spin functions α and β for orbits (such as a and b) which are bonded together, that is, of

reversing the arrows in the vector-bond diagram. The factor $(-1)^R$ equals $+1$ for an even number of reversals, -1 for an odd number.

The Coulomb coefficient

To find the coefficient of the Coulomb integral for two structures, superimpose their vector-bond patterns to form the superposition pattern (Fig. 1). The Coulomb coefficient is 2^{-n} times the sum $(-1)^R$ for the different patterns in which each orbit serves either as the head or as the tail

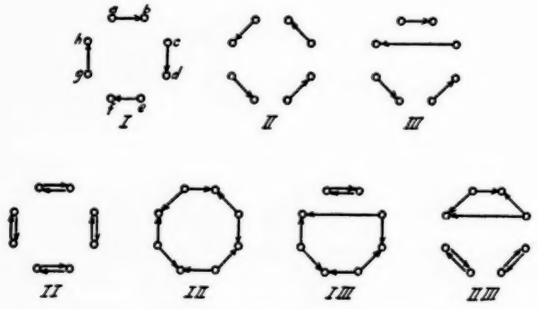

FIG. 1. The vector-bond diagrams for three structures of the canonical set of fourteen for $n=4$, and some of their superposition patterns.

of two arrows which can be made by reversing the arrows, R being the number of reversals. The superposition pattern consists of "islands," or closed polygons formed by an even number of arrows. For each island there are only two satisfactory orientations of the arrows, so that the Coulomb coefficient may be written as $(-1)^r 2^{-(n-i)}$, in which i is the number of islands and r the number of reversals required for an initial satisfactory orientation.

For canonical structures the sign is positive, the Coulomb coefficient being $1/2^{n-i}$. In drawing the superposition pattern for canonical structures the arrows may be replaced by lines.

Coefficients of exchange integrals

Each of the $N!$ permutations may be represented by a permutation diagram, made by drawing an arrow from each orbit in $Pab\cdots e$ to the orbit whose place in $ab\cdots e$ it occupies. Thus if $Pab\cdots e=bd\cdots e$, an arrow is drawn from b to a, from d to b, etc. A closed polygon of arrows is called a cycle of the permutation.[3] A cycle may be called odd if it involves an even number of arrows, otherwise even. The permutation is odd if it contains an odd number of odd cycles; otherwise it is even. The possible permutations are obtained by drawing polygons of arrows in all possible ways such that each orbit is reached by no arrow or by the head of one and the tail of another. The permutation arrows may intersect.

To find the coefficient of a given exchange integral in a matrix element, $(\mathrm{I}/F/P\mathrm{II})$, draw the vector-bond diagram for structure II, change it as indicated by the permutation diagram for P, and form the superposition pattern of I and PII. The coefficient is then given, except for the factor $(-1)^P$, by the above rules for the Coulomb coefficient; that is, it is $(-1)^P(-1)^r 2^{-(n-i)}$.

This procedure may be simplified considerably for single exchange integrals in matrix elements between structures of a canonical set. We first form the superposition pattern of the two structures. If the permutation involves the interchange of orbits in different islands, the number of islands is decreased by one; if the orbits are an odd number of bonds apart in the same island, it is unchanged; if they are an even number apart, it is increased by one. Hence (taking into consideration the factors $(-1)^P$ and $(-1)^r$) it is seen that the coefficient of a single exchange integral for two canonical structures is $2^{-(n-i)}f(p)$, where n is the number of bonds, i is the number of islands in the superposition pattern of the two structures, p the number of bonds in the superposition pattern along the path between the two orbits which are interchanged, and $f(p)$ a factor with the values $-\frac{1}{2}$ for $p=0$, $+1$ for $p=1, 3, 5\cdots$, and -2 for $p=2, 4, 6\cdots$. It is not necessary to use arrows in forming the superposition pattern for canonical structures.

Similar rules may be formulated for more complex permutations.

An example: Six electrons with only spin degeneracy. Placing the six orbits in a ring in the order *abcdef*, the five structures forming a canonical set are those given in Fig. 2. It is seen that

$$\int \mathrm{I}F\mathrm{I}dv = Q+ab+cd+ef-\tfrac{1}{2}ac-\tfrac{1}{2}ad-\tfrac{1}{2}ae-\tfrac{1}{2}af$$
$$-\tfrac{1}{2}bc-\tfrac{1}{2}bd-\tfrac{1}{2}be-\tfrac{1}{2}bf-\tfrac{1}{2}ce-\tfrac{1}{2}cf-\tfrac{1}{2}de-\tfrac{1}{2}df$$
$$+\cdots,$$

[3] The theory of permutation groups is discussed in standard treatises such as W. Burnside, *The Theory of Groups*, Second Edition, Cambridge University Press, 1911.

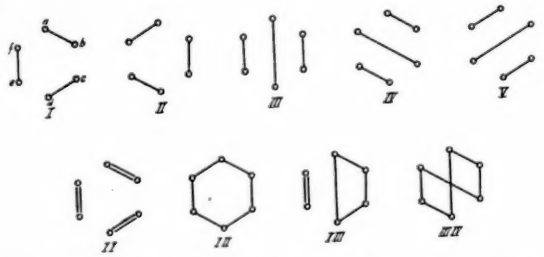

FIG. 2. The five canonical structures for $n=3$, and some of their superposition patterns.

in which Q is the Coulomb integral $(ab\cdots f/F/ab\cdots f)$, ab the single exchange integral $(ab\cdots f/F/ba\cdots f)$, etc. As in this case, it is true in general that in diagonal matrix elements the coefficient of bonding single exchange integrals is $+1$, of nonbonding $-\frac{1}{2}$. From the superposition pattern of I and II we obtain

$$\int I F II\,dv = \tfrac{1}{4}(Q+ab+bc+cd+de+ef+fa+ad+be+cf-2ac-2bd-2ce-2df-2ea-2fb+\cdots),$$

and similar expressions for the other matrix elements can be quickly written.[4] The determination of the coefficients of each of the 720 integrals would be, of course, quite a task, even by this simple method, but any one of them is easily found. Thus from Fig. 3 it is seen that in $\int I F II\,dv$ the coefficient of $(abcdef/F/bcfdae)$ is $-\frac{1}{2}$. The complete matrix for the forty-two independent structures given by ten electrons with only spin degeneracy, retaining only Coulomb and single exchange integrals, can be set up in a few hours.

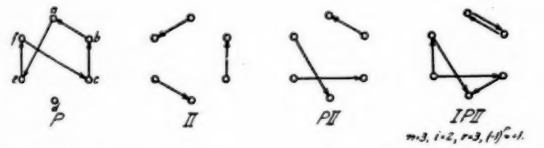

FIG. 3. The permutation diagram for $P\ abcdef=bcfdae$, and the superposition pattern for I PII.

[4] A. Sherman and H. Eyring (J. Am. Chem. Soc. **54**, 2661 (1932)) have published matrix elements for this six-electron system, giving the Coulomb and single exchange integrals. Their coefficients do not show the regularities which our treatment leads to, since their five functions do not form a canonical set.

EXTENSION TO MORE GENERAL SYSTEMS

The foregoing treatment can be extended to states of arbitrary multiplicity by the artifice of including in the system additional electrons and phantom orbits. To represent N electrons and N orbits in states with resultant spin S (multiplicity $2S+1$), form a ring of the real and phantom orbits; a canonical set of electronic structures is then obtained by drawing in all possible ways such that no bonds intersect a phantom bond between each of $2S$ phantom orbits and a real orbit and a real bond between each pair of remaining real orbits. Rules regarding reversal of bond arrows (different numbers of arrow heads on phantom orbits correspond to different M_S values) and the calculation of exchange integral coefficients are easily formulated.

A canonical set of structures for a system with more orbits than electrons is obtained by arranging all the orbits (including phantom orbits for $S>0$) in a ring and then drawing non-intersecting bonds to a number determined by the number of electrons and the multiplicity. If two electrons occupy the same orbit, forming an unshared pair, a loop is drawn with its ends at the orbit.

The bond diagrams provide an obvious simple method of determining the allowed spectral terms for equivalent electrons with Russell-Saunders coupling, which may be convenient for the reason that it separates states of different multiplicity at the start.

The methods developed in this paper have been applied in a discussion of the structure of aromatic substances, free radicals, etc., to be published soon.

The Thermal Decomposition of Ethyl Mercaptan and Ethyl Sulphide

W. M. MALISOFF AND E. M. MARKS, *Atlantic Refining Company, Philadelphia, Pennsylvania*

IN the first issue of this journal (Volume 1, page 77), in their paper with the above title, Trenner and Taylor make several references to our own work on a similar subject. We believe they have misrepresented us on a sufficiently large number of points to give a completely misleading impression of its nature to any one reading their article.

For example, according to Trenner and Taylor: "It has frequently been suggested that the aliphatic mercaptans behave thermally in a manner similar to the amines, and might therefore be suspected of decomposing in a unimolecular manner. In fact, that is the supposed finding of Malisoff and Marks recently for propyl, butyl, amyl and heptyl mercaptans, both iso and normal."

Here is what we say in our summary: "It is impossible with data of this order of accuracy to decide finally between a first and a second-order reaction. The trend is much closer to a first-order reaction and is confirmed by an approximate independence of the rate of decomposition of the concentration used and the simultaneous poor agreement with tests for bimolecularity." And in the body of our article we say "This leaves much room for vacillation in deciding between first and second-order reactions," and we express our doubts in some detail.

According to Trenner and Taylor: " . . . it is hardly surprising that Malisoff and Marks should find no effect from hydrogen and carbon dioxide."

What we said in our summary: "The decomposition of amyl mercaptan is to some extent depressed by the admixture of gases like hydrogen and carbon dioxide." And in the article itself: "It was found that gases like hydrogen and carbon dioxide have no marked effect on the order of magnitude of the amount decomposed."

Our conclusions are "hardly justifiable" because "the intermediate, as has been shown, reacts analytically as a mercaptan." Despite their impression to the contrary Trenner and Taylor have not *shown* the presence of an intermediate; the compound they obtained might have been one, but it might just as well have been a secondary product. And concerning this compound, which is supposed to make the results of our analyses worthless, they themselves say that "as has been shown, a maximum concentration of the intermediate is found in the neighborhood of the point of inflection"—and in this neighborhood, working at pressures of the order of atmospheric, they obtained "small yields," because "its rate of formation is only slightly greater than its rate of decomposition." To secure enough product for an analysis to be made they worked at lower temperature and at *150 atmospheres*. The mercaptans in our experiments were at pressures of the order of 10 millimeters.

The difference between the temperature coefficients found by us and by Trenner and Taylor may be ascribable to other things than our "unjustifiable averaging of numerous erratic results." There is, for one thing, the difference in conditions of experiment, and, for another, the fact that Trenner and Taylor had first to assume that certain points on their curves were "comparable" and then to determine these points by inspection —a process of a rather subjective nature, as can be seen from their Table VI, which contains points of inflection read from Fig. 3. Our values were determined directly from the amount decomposed found by analysis.

Trenner and Taylor talk of our "conclusions that mercaptan decomposition involves a straight split into olefine and hydrogen sulfide in a manner satisfactorily accounted for by a single unimolecular rate." The "straight split" was a suggestion on our part, but was so far from being a conclusion that we spend about a quarter page in discussing a possible chain mechanism.

It is chiefly to this sort of reference by Trenner and Taylor that we object. We make a suggestion concerning the mechanism, a suggestion justified by the experimental results, with full knowledge of its nature as an assumption, and we state that

the evidence favors this rather than the other hypothesis so far advanced. We do not consider it a conclusion, in fact we advance still another hypothesis. But Trenner and Taylor speak of our "conclusions" and "finding," and having thus set up a straw man proceed to demolish him. This seems to us decided misrepresentation, especially as Trenner and Taylor proceed from their supposed refutation to cast doubt upon the validity of our experimental results.

As for the other details of criticism on the page which Trenner and Taylor devote to our results, it is well to realize that this article of theirs deals with the decomposition of ethyl mercaptan in the *absence* of solvents, by a static method, at pressures mostly of the order of several hundred mm, with times of contact of the order of a half hour, at temperatures from 386°−420°. Our experiments were done with different mercaptans, in hydrocarbon diluents where the total mercaptan pressure in the gas was of the order of 10 mm, with times of contact from a few seconds to three minutes, at temperatures from 300° to 475°. We analyzed the products, they simply followed the pressure changes.

It is well to repeat that the title of our paper contains the words "in hydrocarbon solvents" and all our conclusions refer to decomposition under those conditions only. It is quite possible for some of them to diverge from results of Trenner and Taylor without our being entirely incorrect.

The Thermal Decomposition of Ethyl Mercaptan and Ethyl Sulphide. A Reply

NELSON R. TRENNER AND H. AUSTIN TAYLOR, *Department of Chemistry, New York University*

IN reply to the communication of Malisoff and Marks, it is our belief that a detailed perusal of their paper[1] would lead anyone to believe that they had found the decomposition of mercaptans to be (1) entirely homogeneous, (2) a simple split into an olefine and hydrogen sulphide, and (3) of order between one and two, probably closer to the former. Disregarding entirely our suggested mechanism our actual experimental results cannot substantiate these three points and therefore some criticism is justified.

We believe that, accepting the above three points, the logically scientific conclusion would be that the mercaptan decomposition was a unimolecular reaction proceeding in a concentration range where a deviation towards second order had already set in. We believe further that this was the intent of their paper, although in the summary they do not so commit themselves. Why else should they refer to "The unimolecular nature of such decompositions . . . ," "For comparison with other unimolecular reactions . . . ," and finally, "Should it be necessary to invoke chain reactions to explain the speed of such unimolecular reactions . . . ," this latter in spite of the complete absence of any evidence of a chain mechanism?

We demonstrated in our paper that an important feature of mercaptan decomposition lies in the existence of an induction period, markedly affected by surface and foreign gases when the latter were present in amounts comparable with the amount of mercaptan, though not necessarily so in a system already excessively diluted with other foreign gases namely solvent vapors. This induction period increased rapidly with a decrease in initial pressure and should therefore have been quite obvious at the low partial pressure of 10 mm used by Malisoff and Marks.

Regarding their temperature coefficient which they claim was not an averaged value a study of their Fig. 6 will show an energy of activation of 23,000 calories for ten percent decomposition with obviously higher values for fifteen and twenty percent. The value claimed by them is 33,500 calories. A haphazard choice of two other experiments. 7528 and 7463 yields a value of 43,700 calories. Finally it may be added that a decision on mechanism is not necessary to the calculation of a temperature coefficient and since we had found experimentally a comparable point on all our reaction rate curves, our calculation was entirely justified.

In conclusion it would appear from our findings that the effect of ten gases was not such as to alter materially the latter course of the reaction and the assumption therefore that mercaptan decomposition in hydrocarbon solvents would be different from that in the pure state is unjustified.

[1] Malisoff and Marks, Ind. Eng. Chem. 23, 1114 (1931).

The Thermal Decomposition of Ethylene Iodide. Errata

L. B. Arnold, Jr. and G. B. Kistiakowsky, *Chemical Laboratory, Harvard University*

IN the abstract on page 166, Vol. I, February issue of this Journal, "the two reactions are 31,400 cal. and 37,500 cal., respectively." should read, "the two reactions are 30,200 cal. and 36,600 cal., respectively."

On page 169, "an activation energy of 31,400 cal." should read, "an activation energy of 30,200 cal."

Zeeman Effect in Solids. Errata

F. H. Spedding, *Department of Chemistry, University of California*

BECAUSE of an accident in the mails, the author did not personally read the proof of his article in the February issue before it went to press. Therefore the following errors, which ordinarily would have been corrected in the proof, appeared in the publication.

Page 145, col. 2, line 12, read 0.9A° instead of 9.A°.

Page 148, col. 2, second curve from top, the field of 18,500 gauss was parallel to the "a" axis of the crystal. In all other curves on the page it was parallel to the "c" axis.

Page 149, col. 1, third line from bottom, read "g" factors instead of three factors.

Pages 151 and 152, read "a" axis instead of "d" axis.

Page 153, above curves in col. 1, insert light ray parallel to "b" axis. Above column 2 light ray parallel to "c" axis.

Page 153. The lower spectrum is reversed and should be turned end for end to correspond with the spectrum with zero field.

LETTERS TO THE EDITOR

Editorial

In response to requests from our contributors, and after a canvass of the opinions of the editorial board, the *Journal of Chemical Physics* wishes to announce that a "Letters to the Editor" section will be carried by the Journal in the future. This section will accept reports of new work, provided these are terse and contain few figures and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents.

Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual page charge ($3.00 per page) will not be made and no reprints will be furnished free.

HAROLD C. UREY
Managing Editor

The Isotopic Fractionation of Water*

When water is subjected to electrolysis an isotopic fractionation occurs (Washburn and Urey, Proc. Nat. Acad. Sci. **18**, 496 (1932)). It has been found that the heavier isotope of hydrogen and the heavier isotopes of oxygen are concentrated in the residual water. The specific gravity of the residual water rises continuously as the electrolysis proceeds. The rise in specific gravity is accompanied by a rise in the freezing point and in the boiling point and by a decrease in the refractive index. Thus for water of specific gravity 1.0014, the changes are; F.P., $+0.050°C$; B.P., $+0.02°C$; n_D^{25}, $-(60\pm2)\times10^{-6}$.

No indication of approach to an electrolysis equilibrium has been found and there is every reason to hope that it will be possible to obtain the various isotopes of hydrogen and oxygen in a pure state, certainly in highly concentrated form.

If the oxygen from the electrolysis of normal water is combined with normal hydrogen, the water produced has a lower specific gravity than normal water. If this water be again partially electrolyzed and the oxygen combined again with normal hydrogen, a further drop in the specific gravity of the water occurs, the total drop thus far obtained being 18 parts per million. It will consequently be possible to prepare isotopically pure water of the composition $H^1O^{16}H^1$ and hence to determine accurately the atomic weight of normal oxygen on the $O^{16}=16$ scale.

With the different isotopes of hydrogen and oxygen available in pure form, a new field of chemistry and possibly also of biology will be opened up, since the different isotopes of hydrogen, at least, may be expected to exhibit pronounced differences in chemical behavior.

A survey is being made of water from different natural sources to find out whether differences in isotopic composition occur in nature.

EDWARD W. WASHBURN
EDGAR R. SMITH
MIKKEL FRANDSEN

Washington, D. C.
March 6, 1933

* Published by permission of the Acting Director of the Bureau of Standards, Department of Commerce.